# Hess's Law 

Calorimetry is an accurate technique for determining enthalpy changes. But what if a reaction is:

- too dangerous to perform in a lab
- too slow to perform in a lab
- impossible to perform in a calorimeter


## Other Techniques

- Aside from calorimetry ( $q=m c T$ ), scientists can use the following to determine enthalpy changes.
- Hess's law
- Enthalpy of Formation data


## Hess's Law of Summation

For any reaction that can be written in steps, the $\Delta \mathrm{H}^{\circ}$ is the same as the sum of the values of the $\Delta H^{\circ}$ for each individual step.

Potential Energy Diagram Showing Additive Enthalpy Changes


## Rule \#1

$$
\begin{aligned}
& \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \rightarrow 2 \mathrm{NO}_{2}(\mathrm{~g}) \Delta \mathrm{H}^{\circ}=+57.93 \mathrm{~kJ} \\
& 2 \mathrm{NO}_{2}(\mathrm{~g}) \rightarrow \mathrm{N}_{2} \mathrm{O}_{4}(\mathrm{~g}) \square
\end{aligned}
$$

1. Reversing a chemical reaction causes a sign change in front of the $\Delta \mathrm{H}^{\circ}$ value.

## Rule \#2

2. If the coefficients of a chemical equation are altered by multiplying or dividing then the $\Delta \mathrm{H}$ is altered the same way
$\mathrm{C}_{2} \mathrm{H}_{2}+5 / 2 \mathrm{O}_{2} \rightarrow \mathrm{CO}_{2}+\mathrm{H}_{2} \mathrm{O}$
$2 \mathrm{C}_{2} \mathrm{H}_{2}+5 \mathrm{O}_{2} \rightarrow 2 \mathrm{CO}_{2}+2 \mathrm{H}_{2} \mathrm{O} \quad \Delta \mathrm{H}=-2598 \mathrm{~kJ}$

## Rule \#3

## 3. When cancelling compounds

 for Hess's Law, the state of the compounds is important.$$
\begin{aligned}
& \mathrm{H}_{2(\mathrm{~g})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{H}_{2} \mathrm{O}_{(\mathrm{g})} \Delta \mathrm{H}^{\circ}=+57.93 \mathrm{~kJ} \\
& \mathrm{~K}_{2} \mathrm{SO}_{4(\mathrm{~s})}+2 \mathrm{H}_{2} \mathrm{O}_{(\mathrm{l})} \rightarrow \mathrm{H}_{2} \mathrm{SO}_{4(\mathrm{aq})}+ 2 \mathrm{KOH}_{(\mathrm{s})} \\
& \Delta \mathrm{H}^{\circ}=+342.4 \mathrm{~kJ}
\end{aligned}
$$

These two CANNOT cancel each other out

## $\Delta H^{\circ}$ Rules

1. If all the coefficients of an eq ${ }^{n}$ are multiplied or divided by a common factor, the $\Delta \mathrm{H}^{\circ}$ must be changed likewise.
2. When a reaction is reversed, the sign of $\Delta \mathrm{H}^{\circ}$ must also be reversed.
3. When cancelling compounds for Hess's Law, the state of the compounds is important.

## Enthalpy

$\Delta \mathrm{H}^{\circ}$ values of unknown reactions can be solved when other known reactions are given.

## Example \#1

$$
\mathrm{C}_{(s)}+\mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{2(\mathrm{~g})} \Delta \mathrm{H}^{\circ}=?
$$

$\mathrm{C}_{(\mathrm{s})}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{(\mathrm{g})} \Delta \mathrm{H}^{\circ}=-110.5 \mathrm{~kJ}$
$\mathrm{CO}_{(g)}+1 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{CO}_{2(\mathrm{~g})} \Delta \mathrm{H}^{\circ}=-283.0 \mathrm{~kJ}$
$\mathrm{C}_{(\mathrm{s})}+\mathrm{O}_{2(g)} \rightarrow \mathrm{CO}_{2(g)} \quad \Delta \mathrm{H}^{\circ}=-393.5 \mathrm{~kJ}$

## Example \#2

$2 \mathrm{Fe}_{(\mathrm{s})}+3 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})} \Delta \mathrm{H}^{\circ}=$ ?
$\mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})}+3 \mathrm{CO}_{(\mathrm{g})} \rightarrow 2 \mathrm{Fe}_{(\mathrm{s})}+3 \mathrm{CO}_{2(\mathrm{~g})} \Delta \mathrm{H}^{\circ}=-26.7 \mathrm{~kJ}$
Flip! $2 \mathrm{Fe}_{(\mathrm{s})}+3 \mathrm{CQ}_{2(\mathrm{~g})} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})}+3 \mathrm{CO}_{(\mathrm{g})} \quad \Delta \mathrm{H}^{\circ}=+26.7 \mathrm{~kJ}$

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

$x 3!3 \mathrm{CQ}_{(\mathrm{g})}+3 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow 3 \mathrm{CQ}_{2(\mathrm{~g})}$
$2 \mathrm{Fe}_{(\mathrm{s})}+3 / 2 \mathrm{O}_{2(\mathrm{~g})} \rightarrow \mathrm{Fe}_{2} \mathrm{O}_{3(\mathrm{~s})} \quad \Delta \mathrm{H}^{\circ}=-822.3 \mathrm{~kJ}$

