Hess's Law and the Additivity of Heats
Hess's Law: The value of $\Delta H$ for any reaction that can be written in steps equals the sum of the values of $\Delta H$ for the individual steps.

## Method 1: Additivity of Heats

1. Identify the target equation and balanced it (if not given).
2. Identify the individual step equations. These are provided or are found on a Table of Heats of Formation.
3. Reverse any step equations so that the position of reactants/products matches that of the target equation. If an equation is reversed, also reverse the sign of $\Delta H$ for the step equation.
4. Multiply the step equations by the appropriate coefficient to match those in the target equation. Also multiply the $\Delta H$ by the same coefficient.
5. Add up the modified step equations and their $\Delta H$ values. The sum of the modified individual step equation should be identical to the target equation.

| Heats (Enthalpy Change) of Formation |  |  |  |
| :---: | :---: | :---: | :---: |
| Elements | Formula | Name | $\Delta H(\mathrm{~kJ} / \mathrm{mol})$ |
| $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$ | water vapour | - 241.8 |
| $\mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{l})$ | water | - 285.8 |
| $\mathrm{S}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{SO}_{2}(\mathrm{~g})$ | sulfur dioxide | - 296.8 |
| $\mathrm{S}(\mathrm{s})+3 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{SO}_{3}(\mathrm{~g})$ | sulfur trioxide | -395.7 |
| $\mathrm{H}_{2}(\mathrm{~g})+\mathrm{S}(\mathrm{s})+2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{I})$ | sulfuric acid | - 811.7 |
| $1 / 2 \mathrm{~N}_{2}(\mathrm{~g})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{NO}(\mathrm{g})$ | nitric oxide | +90.25 |
| $1 / 2 \mathrm{~N}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{NO}_{2}(\mathrm{~g})$ | nitrogen dioxide | + 33.18 |
| $1 / 2 \mathrm{~N}_{2}(\mathrm{~g})+3 / 2 \mathrm{H}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{NH}_{3}(\mathrm{~g})$ | ammonia | - 46.11 |
| $\mathrm{C}(\mathrm{s})+1 / 2 \mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CO}(\mathrm{g})$ | carbon monoxide | - 110.5 |
| $\mathrm{C}(\mathrm{s})+\mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CO}_{2}(\mathrm{~g})$ | carbon dioxide | - 393.5 |
| $\mathrm{C}(\mathrm{s})+2 \mathrm{H}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CH}_{4}(\mathrm{~g})$ | methane | - 74.81 |
| $2 \mathrm{C}(\mathrm{s})+3 \mathrm{H}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{C}_{2} \mathrm{H}_{6}$ (g) | ethane | - 84.68 |
| $3 \mathrm{C}(\mathrm{s})+4 \mathrm{H}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{C}_{3} \mathrm{H}_{8}(\mathrm{~g})$ | propane | - 103.8 |
| $1 / 2 \mathrm{H}_{2}(\mathrm{~g})+1 / 2 \mathrm{I}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{HI}(\mathrm{g})$ | hydrogen iodide | + 25.9 |
| $4 \mathrm{C}(\mathrm{s})+4 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}$ (I) | butyric acid | - 522.1 |
| $2 \mathrm{C}(\mathrm{s})+2 \mathrm{H}_{2}(\mathrm{~g})+\mathrm{O}_{2}(\mathrm{~g})$ | $\rightarrow \mathrm{CH}_{3} \mathrm{COOH}$ (I) | acetic acid | - 486.6 |

## Method 1: Additivity of Heats (continued)

Example: Determine $\Delta H$ for the following reaction:
methane $(\mathrm{g})$ + oxygen $(\mathrm{g}) \longrightarrow$ carbon dioxide $(\mathrm{g})+$ water $(\mathrm{g})$

## Method 2: Summation of Heats

Identify the $\Delta H_{\text {formation }}$ for each product and reactant and solve using the equation:

$$
\Delta H=\sum\left(n \Delta H_{\text {form }}(\text { products })\right)-\sum\left(n \Delta H_{\text {form }}(\text { reactants })\right.
$$

Example: Determine $\Delta H$ for the following reaction:
ammonia (g) + oxygen (g) $\longrightarrow$ nitrogen dioxide (g) + water (g)
$\mathrm{NH}_{3}(\mathrm{~g})+7 / 4 \mathrm{O}_{2} \longrightarrow \mathrm{NO}_{2}(\mathrm{~g}) \quad+3 / 2 \mathrm{H}_{2} \mathrm{O}(\mathbf{g})$

## Hess's Law and Additivity of Heats

Complete these questions using the Additivity of Heats method. Refer to the Table of Heats of Formation for the individual step equations.

1. Calculate $\Delta H$ for each of the following:
a) $\mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longrightarrow \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
b) $\mathrm{C}_{3} \mathrm{H}_{7} \mathrm{COOH}(\mathrm{I})+5 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 4 \mathrm{CO}_{2}(\mathrm{~g})+4 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
c) $3 \mathrm{CH}_{3} \mathrm{COOH}(\mathrm{I})+11 / 2 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow 5 \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{CO}(\mathrm{g})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{I})$
2. a) Write a balanced equation for the combustion of propane gas $\left(\mathrm{C}_{3} \mathrm{H}_{8}\right)$ to produce carbon dioxide and water vapour.
b) Add equations and heats of formation to calculate the $\Delta H$ for the combustion of 1.00 mol of propane.

Answers: 1 a) $44.0 \mathrm{~kJ} / \mathrm{mol}$
b) $-2195 \mathrm{~kJ} / \mathrm{mol}$
c) $-2333 \mathrm{~kJ} / \mathrm{mol}$

2 -2044 kJ

Do the following problems using the Summation of Heats method.

1. Predict the heat of reaction for:
$\mathrm{CH}_{4}(\mathrm{~g})+2 \mathrm{O}_{2}(\mathrm{~g}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+2 \mathrm{H}_{2} \mathrm{O}(\mathrm{g})$
2. Given that $\Delta H_{\text {form }}$ for $\mathrm{SiO}_{2}(\mathrm{~s})$ is $-856.9 \mathrm{~kJ} / \mathrm{mol}$, what is the $\Delta H$ for:

$$
\mathrm{SiO}_{2}(\mathrm{~s})+\mathrm{C}(\mathrm{~s}) \longrightarrow \mathrm{CO}_{2}(\mathrm{~g})+\mathrm{Si}(\mathrm{~s})
$$

3. What is the heat of formation of $\mathrm{H}_{2} \mathrm{SO}_{4}(\mathrm{I})$ from $\mathrm{H}_{2} \mathrm{O}(\mathrm{I})$ and $\mathrm{SO}_{3}(\mathrm{~g})$ ?
4. Given: $\quad \Delta H_{\text {form }}$ for $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})=-3009.5 \mathrm{~kJ} / \mathrm{mol}$ $\Delta H_{\text {form }}$ for $\mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{~s})=-1266.5 \mathrm{~kJ} / \mathrm{mol}$

Calculate the heat of reaction for: $\mathrm{P}_{4} \mathrm{O}_{10}(\mathrm{~s})+6 \mathrm{H}_{2} \mathrm{O}(\mathrm{I}) \longrightarrow 4 \mathrm{H}_{3} \mathrm{PO}_{4}(\mathrm{~s})$
Answers: $1 .-802.3 \mathrm{~kJ} / \mathrm{mol}$
2. $+463.4 \mathrm{~kJ} / \mathrm{mol}$
3. $-130.2 \mathrm{~kJ} / \mathrm{mol}$
4. $-342 \mathrm{~kJ} / \mathrm{mol}$

