

9.10: Determining Enthalpies of Reaction from Standard Enthalpies of Formation

We have examined how to measure ΔH for a chemical reaction directly through calorimetry and how to infer ΔH for a reaction from related reactions through Hess's law. We have also seen how to estimate ΔH for a reaction from bond energies. We now turn to a fourth and more convenient way to determine ΔH for a large number of chemical reactions: from tabulated *standard enthalpies of formation*.

Standard States and Standard Enthalpy Changes

Recall that ΔH is the *change* in enthalpy for a chemical reaction—the difference in enthalpy between the products and the reactants. Because we are interested in changes in enthalpy (and not in absolute values of enthalpy itself), we are free to define the *zero* of enthalpy as conveniently as possible. Returning to our mountain-climbing analogy from Section 9.3., a change in altitude (like a change in enthalpy) is an absolute quantity. Altitude itself (like enthalpy), however, is a relative quantity, defined relative to some standard (such as sea level in the case of altitude). We define a similar, albeit slightly more complex, standard for enthalpy. This standard has three parts: the standard state \mathcal{P} , the standard enthalpy change $(\Delta H^{\circ})^{\mathcal{P}}$, and the standard enthalpy (or heat) of formation $(\Delta H^{\circ}_{\mathbf{f}})^{\mathcal{P}}$.

1. Standard State

- For a Gas: The standard state for a gas is the pure gas at a pressure of exactly 1 atm.
- For a Liquid or Solid: The standard state for a liquid or solid is the pure substance in its most stable form at a pressure of 1 atm and at the temperature of interest (often taken to be 25 °C).
- For a Substance in Solution: The standard state for a substance in solution is a concentration of exactly 1 M.

2. Standard Enthalpy Change (ΔH°)

 The change in enthalpy for a process when all reactants and products are in their standard states. The degree sign indicates standard states.

3. Standard Enthalpy of Formation (ΔH_f)

- For a Pure Compound: The change in enthalpy when 1 mol of the compound forms from its constituent elements in their standard states.
- lacksquare For a Pure Element in Its Standard State: $\Delta H_{
 m f}^{\,\circ}=0$

The standard state was changed in 1997 to a pressure of 1 bar, which is very close to 1 atm $(1~\rm{atm}=1.013~\rm{bar})$ Both standards are now in common use.

The standard enthalpy of formation is also called the **standard heat of formation** .

Assigning the value of zero to the standard enthalpy of formation for an element in its standard state is the equivalent of assigning an altitude of zero to sea level. Once we assume sea level is zero, we can measure all subsequent changes in altitude relative to sea level. Similarly, we can measure all changes in enthalpy relative to those of pure elements in their standard states.

For example, consider the standard enthalpy of formation of methane gas at 25 $^{\circ}\text{C}\textsc{:}$

$$ext{C(s, graphite)} + 2 ext{ H}_2\left(g
ight)
ightarrow ext{CH}_4\left(g
ight) \hspace{0.2in} \Delta H_{ ext{f}}^{^{\circ}} = -74.6 ext{ kJ/mol}$$

The carbon in this equation must be graphite (the most stable form of carbon at 1 atm and $25\,^{\circ}$ C).

For methane, as with most compounds, $\Delta H_{\rm f}^*$ is negative. Continuing our analogy, if we think of pure elements in their standard states as being at *sea level*, then most compounds lie *below sea level*. We always write the chemical equation for the enthalpy of formation of a compound to form 1 mol of the compound, so $\Delta H_{\rm f}^*$ has the units of kJ/mol. Table 9.4 lists $\Delta H_{\rm f}^*$ values for selected compounds. A more comprehensive list is in Appendix IIB.

Table 9.4 Standard Enthalpies (or Heats) of Formation, ΔH_{f} , at 298 K

Formula	$\Delta H_{ m f}^{\circ}({ m kJ/mol})$	Formula	$\Delta H_{ m f}^{\circ}({ m kJ/mol})$	Formula
Bromine		C ₃ H ₈ O(<i>I</i> , isopropanol)	-318.1	Oxygen
Br(g)	111.9	C ₆ H ₆ (1)	49.1	O ₂ (g)
Br ₂ (1)	0	C ₆ H ₁₂ O ₆ (s, glucose)	-1273.3	O ₃ (g)
HBr(g)	-36.3	C ₁₂ H ₂₂ O ₁₁ (<i>s</i> , sucrose)	-2226.1	H ₂ O(<i>g</i>)
Calcium		Chlorine		H ₂ O(<i>I</i>)
Ca(s)	0	CI(g)	121.3	Silver
CaO(s)	-634.9	Cl ₂ (g)	0	Ag(s)
CaCO ₃ (s)	-1207.6	HCI(g)	-92.3	AgCI(s)
Carbon	,),	Fluorine		Sodium
C(s, graphite)	0	F(g)	79.38	Na(s)
C(s, diamond)	1.88	F ₂ (g)	0	Na(g)
CO(g)	-110.5	HF(g)	-273.3	NaCI(s)
CO ₂ (g)	-393.5	Hydrogen		Na ₂ CO ₃ (s)
CH ₄ (g)	-74.6	H(g)	218.0	NaHCO ₃ (s)
CH ₃ OH(I)	-238.6	H ₂ (<i>g</i>)	0	Sulfur
$C_2H_2(g)$	227.4	Nitrogen		S ₈ (s, rhombic)
C ₂ H ₄ (<i>g</i>)	52.4	N ₂ (g)	0	S ₈ (s, monoclinic)
C ₂ H ₆ (<i>g</i>)	-84.68	NH ₃ (<i>g</i>)	-45.9	SO ₂ (g)
C ₂ H ₅ OH(I)	-277.6	NH ₄ NO ₃ (s)	-365.6	SO ₃ (g)
C ₃ H ₈ (<i>g</i>)	-103.85	NO(g)	91.3	H ₂ SO ₄ (I)
C ₃ H ₆ O(<i>I</i> , acetone)	-248.4	N ₂ O(<i>g</i>)	81.6	

Example 9.11 Standard Enthalpies of Formation

Write equations for the formation of (a) MgCO₃ (s)and (b) $C_6H_{12}O_6$ (s)from their respective elements in their standard states. Include the value of $\Delta H_{\rm f}$ for each equation.

SOLUTION

(a)MgCO₃(s)

Write the equation with the constituent elements in ${\rm MgCO_3}$ in their standard states as the reactants and 1 mol of ${\rm MgCO_3}$ as the product.

Balance the equation and look up $\Delta H_{\rm f}^{^{*}}$ in Appendix IIB. (Use fractional coefficients so that the product of the reaction is 1 mol of MgCO₃)

$$\operatorname{Mg}(s) + \operatorname{C}(s, \operatorname{graphite}) + \operatorname{O}_2(g) \to \operatorname{MgCO}_3(s)$$

$$\mathrm{Mg}\left(s\right)+\mathrm{C}\left(s,\mathrm{graphite}\right)+\frac{3}{2}\mathrm{O}_{2}\left(g\right)\rightarrow\mathrm{MgCO}_{3}\left(s\right)\quad\Delta H_{\mathrm{f}}^{^{\ast}}=-1095.8\:\mathrm{kJ/mol}$$

(b) $C_6H_{12}O_6(s)$

Write the equation with the constituent elements in $C_6H_{12}O_6$ in their standard states as the reactants and 1 mol of $C_6H_{12}O_6$ as the product.

Balance the equation and look up $\Delta H_{\rm f}^{\circ}$ in Appendix IIB.

$$\mathrm{C}\left(s,\mathrm{graphite}
ight) + \mathrm{H}_{2}\left(g
ight) + \mathrm{O}_{2}\left(g
ight)
ightarrow \mathrm{C}_{6}\mathrm{H}_{12}\mathrm{O}_{6}\left(s
ight)$$

FOR PRACTICE 9.11 Write equations for the formation of (a) NaCl(s) and (b) $Pb(NO_3)_2(s)$ from their respective elements in their standard states. Include the value of ΔH_t for each equation.

Calculating the Standard Enthalpy Change for a Reaction

We have just seen that the standard enthalpy of formation corresponds to the *formation* of a compound from its constituent elements in their standard states:

$$ho$$
 elements $ightarrow$ compound $\Delta H_{
m f}$

Therefore, the *negative* of the standard enthalpy of formation corresponds to the *decomposition* of a compound into its constituent elements in their standard states:

compound
$$ightarrow$$
 elements $-\Delta H_{
m f}^{\, \circ}$

We can use these two concepts—the decomposition of a compound into its elements and the formation of a compound from its elements—to calculate the enthalpy change of any reaction by mentally taking the reactants through two steps. In the first step we *decompose the reactants* into their constituent elements in their standard states; in the second step we *form the products* from the constituent elements in their standard states:

$$\begin{array}{ll} \text{reactants} & \longrightarrow \text{elements} & \Delta H_1 = -\Sigma \Delta H_\mathrm{f}^\circ \text{(reactants)} \\ \\ \text{elements} & \longrightarrow \text{products} & \Delta H_2 = +\Sigma \Delta H_\mathrm{f}^\circ \text{(products)} \\ \\ \hline \text{reactants} & \longrightarrow \text{products} & \Delta H_\mathrm{rxn}^\circ = \Delta H_1 + \Delta H_2 \end{array}$$

In these equations, Σ means "the sum of" so that ΔH_1 is the sum of the negatives of the heats of formation of the reactants and ΔH_2 is the sum of the heats of formation of the products.

We can demonstrate this procedure by calculating the standard enthalpy change $(\Delta H_{\rm rxn})$ for the combustion of methane:

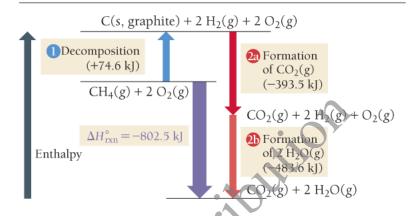
$$ext{CH}_4\left(g
ight) + 2 ext{ O}_2\left(g
ight)
ightarrow ext{CO}_2\left(g
ight) + 2 ext{ H}_2 ext{O}\left(g
ight) \quad \Delta H_{ ext{ryn}}^{\circ} = ?$$

The enthalpy changes associated with the decomposition of the reactants and the formation of the products are shown in Figure 9.11. The first step (1) is the decomposition of 1 mol of methane into its constituent elements in their standard states. We can obtain the change in enthalpy for this step by reversing the enthalpy of formation equation for methane and changing the sign of ΔH_{ϵ} :

$$(1)~\mathrm{CH_4}\left(g\right) \rightarrow \mathrm{C}\left(\mathrm{s,\,graphite}\right) + 2~\mathrm{H_2}\left(g\right) ~~ -\Delta H_\mathrm{f}^{^{\circ}} = +74.6~\mathrm{kJ/mol}$$

Figure 9.11 Calculating the Enthalpy Change for the Combustion of Methane

Calculating the Enthalpy Change for the Combustion of Methane



The second step, the formation of the products from their constituent elements, has two parts: (2a) the formation of 1 mol CO_2 and (2b) the formation of 2 mol H_2O . Because part (2b) forms 2 mol H_2O , we multiply the ΔH_1^+ for that step by 2:

$$\begin{array}{ll} \text{(2a) C(s, graphite)} + \text{O}_2\left(g\right) \to \text{CO}_2\left(g\right) & \Delta H_{\text{f}}^{\; \cdot} = -393.5 \; \text{kJ/mol} \\ \text{(2b) } 2 \times \left[\text{H}_2\left(g\right) + \frac{1}{2}\text{O}_2\left(g\right) \to \text{H}_2\text{O}\left(g\right)\right] & 2 \times \Delta H_{\text{f}}^{\; \cdot} = 2 \times \left(-241.8 \; \text{kJ/mol}\right) \end{array}$$

As we know from Hess's law, the enthalpy of reaction for the overall reaction is the sum of the enthalpies of reaction of the individual steps:

$$\begin{array}{ll} \text{(1) CH}_4(g) & \longrightarrow C(s, \text{graphite}) + 2 \, \text{H}_2(g) & -\Delta H_{\rm f}^{\circ} = +74.6 \, \text{kJ/mol} \\ \text{(2a) } C(s, \text{graphite}) + {\rm O}_2(g) & \Delta H_{\rm f}^{\circ} = -393.5 \, \text{kJ/mol} \\ \\ \text{(2b) } 2 \, \text{H}_2(g) + {\rm O}_2(g) & 2 \times \Delta H_{\rm f}^{\circ} = -483.6 \, \text{kJ/mol} \\ \\ \hline \text{CH}_4(g) + 2 \, {\rm O}_2(g) & \longrightarrow {\rm CO}_2(g) + 2 \, {\rm H}_2{\rm O}(g) & \Delta H_{\rm rxn}^{\circ} = -802.5 \, \text{kJ/mol} \\ \end{array}$$

We can streamline and generalize this process as follows:

To calculate ΔH_{rxtr} subtract the enthalpies of formation of the reactants multiplied by their stoichiometric coefficients from the enthalpies of formation of the products multiplied by their stoichiometric coefficients.

In the form of an equation,

$$\Delta H_{
m rxn}^{"} = \Sigma n_{
m p} \Delta H_{
m f}^{"} \left({
m products}
ight) - \Sigma n_{
m r} \Delta H_{
m f}^{"} \left({
m reactants}
ight)$$

In this equation, $n_{\rm p}$ represents the stoichiometric coefficients of the products, $n_{\rm r}$ represents the stoichiometric coefficients of the reactants, and $\Delta H_{\rm f}^*$ represents the standard enthalpies of formation. Keep in mind when using this equation that elements in their standard states have $\Delta H_{\rm f}^*=0$ Examples 9.12 and 9.13 demonstrate this process.

Example 9.12 $\Delta H_{\mathrm{rxn}}^{\circ}$ and Standard Enthalpies of Formation

Use the standard enthalpies of formation to determine $\Delta H_{\mathrm{rxn}}^{\circ}$ for the reaction.

$$4~\mathrm{NH_3}\left(g\right) + 5~\mathrm{O_2}\left(g\right) \rightarrow 4~\mathrm{NO}\left(g\right) + 6~\mathrm{H_2O}\left(g\right)$$

SORT You are given the balanced equation and asked to find the enthalpy of reaction.

GIVEN: $4~\mathrm{NH_3}\left(g\right) + 5~\mathrm{O_2}\left(g\right) \rightarrow 4~\mathrm{NO}\left(g\right) + 6~\mathrm{H_2O}\left(g\right)$

FIND: $\Delta H_{\rm rxn}$

STRATEGIZE To calculate $\Delta H_{\rm rxn}^{\circ}$ from standard enthalpies of formation, subtract the heats of formation of the reactants multiplied by their stoichiometric coefficients from the heats of formation of the products multiplied by their stoichiometric coefficients.

CONCEPTUAL PLAN

$$\Delta H_{\mathrm{rxn}}^{"} = \Sigma n_{\mathrm{p}} \Delta H_{\mathrm{f}}^{"} \left(\mathrm{products} \right) - \Sigma n_{\mathrm{r}} \Delta H_{\mathrm{rxn}}^{"} \left(\mathrm{reactants} \right)$$

SOLVE Begin by looking up (in Appendix IIB \square) the standard enthalpy of formation for each reactant and product. Remember that the standard enthalpy of formation of pure elements in their standard state is zero. Calculate $\Delta H_{\text{rxn}}^{-}$ by substituting into the equation.

SOLUTION

Reactant or product	$\Delta H_{ m f}^{\circ}({ m kJ/mol},$ from Appendix IIB)
NH ₃ (g)	-45.9
O ₂ (g)	0.0
NO(g)	+91.3
$H_2O(g)$	-241.8

$$\begin{array}{lll} \Delta H_{\rm rxn}^{^{*}} &=& \Sigma n_{\rm p} \Delta H_{\rm f}^{^{*}} \left({\rm products} \right) - \Sigma n_{\rm r} \Delta H_{\rm f}^{^{*}} \left({\rm reactants} \right) \\ &=& \left[4 \left(\Delta H_{\rm f, NO(g)}^{^{*}} \right) + 6 \left(\Delta H_{\rm f, H_2O(g)}^{^{*}} \right) \right] - \left[4 \left(\Delta H_{\rm f, NH_3(g)}^{^{*}} \right) + 5 \left(\Delta H_{\rm f, O_2(g)}^{^{*}} \right) \right] \\ &=& \left[4 (+91.3 \; {\rm kJ}) + 6 \left(-241.8 \; {\rm kJ} \right) \right] - \left[4 (-45.9 \; {\rm kJ}) + 5 \left(0.0 \; {\rm kJ} \right) \right] \\ &=& -1085.6 \; {\rm kJ} - \left(-183.6 \; {\rm kJ} \right) \\ &=& -902.0 \; {\rm kJ} \end{array}$$

CHECK The units of the answer (kJ) are correct. The answer is negative, which means that the reaction is exothermic.

FOR PRACTICE 9.12 The thermite reaction, in which powdered aluminum reacts with iron(III) oxide, is highly exothermic.

$$2 ext{ Al}\left(s
ight) + ext{Fe}_2 ext{O}_3\left(s
ight)
ightarrow ext{Al}_2 ext{O}_3\left(s
ight) + 2 ext{Fe}\left(s
ight)$$

Use standard enthalpies of formation to find $\Delta H_{\mathrm{rxn}}^{^{\circ}}$ for the thermite reaction.



The reaction of powdered aluminum with iron(III) oxide, known as the thermite reaction, releases a large amount of heat.

Interactive Worked Example 9.12 ΔH_{rxn}° and Standard Enthalpies of Formation

Example 9.13 $\Delta H_{\mathrm{rxn}}^{^{\circ}}$ and Standard Enthalpies of Formation

A city of 100,000 people uses approximately 1.0×10^{11} kJof energy per day. Suppose all of the city's energy comes from the combustion of liquid octane (C_8H_{18}) to form gaseous water and gaseous carbon dioxide. Use standard enthalpies of formation to calculate ΔH_{rxn}^* for the combustion of octane and determine how many kilograms of octane are necessary to provide this amount of energy.

SORT You are given the amount of energy used and asked to find the mass of octane required to produce the energy.

GIVEN: $1.0 \times 10^{11} \text{ kJ}$

FIND: kg C₈H₁₈

STRATEGIZE The conceptual plan has three parts. In the first part, write a balanced equation for the combustion of octane.

In the second part, calculate $\Delta H_{\mathrm{rxn}}^{\circ}$ from the $\Delta H_{\mathrm{f}}^{\circ}$ values of the reactants and products.

In the third part, convert from kilojoules of energy to moles of octane using the conversion factor found in part 2, and then convert from moles of octane to mass of octane using the molar mass.

CONCEPTUAL PLAN

- 1. Write balanced equation.
- 2.

 $\Delta H_{\rm f}^{\circ}$ s $\Delta H_{\rm rxn}^{\circ}$

RELATIONSHIPS USED

 $molar\;mass\;C_8H_{18}=114.22\;g/mol$

 $1~\mathrm{kg} = 1000~\mathrm{g}$

SOLVE Begin by writing the balanced equation for the combustion of octane. For convenience, do not clear the $\frac{25}{2}$ fraction in order to keep the coefficient on octane as 1.

SOLUTION PART 1

$$\mathrm{C_8H_{18}}\left(l\right) + \frac{25}{2}\mathrm{O_2}\left(g\right) \rightarrow 8\;\mathrm{CO_2}\left(g\right) + 9\;\mathrm{H_2O}\left(g\right)$$

Look up (in Appendix IIB \Box) the standard enthalpy of formation for each reactant and product and calculate $\Delta H_{\rm rxn}$.

SOLUTION PART 2

Reactant or product	$\Delta H_{ m f}^{\circ}$ (kJ/mol, from Appendix IIB)
C ₈ H ₁₈ (/)	-250.1
$O_2(g)$	0.0
$CO_2(g)$	-393.5
$H_2O(g)$	-241.8

$$\begin{array}{lll} \Delta H_{\rm rxn}^{"} &=& \sum n_{\rm P} \Delta H_{\rm f} \; ({\rm products}) - \sum n_{\rm r} \Delta H_{\rm f}^{"} \; ({\rm reactants}) \\ &=& \left[8 \left(\Delta H_{\rm f,\,CO_2(g)} \right) + 9 \left(\Delta H_{\rm f,\,H_2O(g)} \right) \right] - \left[1 \left(\Delta H_{\rm f,\,C_8H_{18}(l)} \right) + \frac{25}{2} \left(\Delta H_{\rm f,\,O_2(g)} \right) \right] \\ &=& \left[8 (-393.5 \; {\rm kJ}) + 9 \left(-241.8 \; {\rm kJ} \right) \right] - \left[1 \left(-250.1 \; {\rm kJ} \right) + \frac{25}{2} \left(0.0 \; {\rm kJ} \right) \right] \\ &=& -5324.2 \; {\rm kJ} - \left(-250.1 \; {\rm kJ} \right) \\ &=& -5074.1 \; {\rm kJ} \end{array}$$

From parts 1 and 2 of the conceptual plan, build a conversion factor between mol C_8H_{18} and kJ.

Follow part 3 of the conceptual plan. Begin with -1.0×10^{11} kJ(because the city uses this much energy, the reaction must emit this amount, and therefore the sign is negative) and follow the steps to determine kg octane.

SOLUTION PART 3

$$1 \text{ mol } C_8H_{18}: -5074.1 \text{ kJ}$$

$$-1.0\times10^{11}\text{ keV}\times\frac{1\text{ mol }C_8H_{18}}{-5074.1\text{ keV}}\times\frac{114.22\text{ g/}C_8H_{18}}{1\text{ mol }C_8H_{18}}\times\frac{1\text{ kg}}{1000\text{ g/}}=2.3\times10^6\text{ kg }C_8H_{18}$$

CHECK The units of the answer (kg C_8H_{18})are correct. The answer is positive, as it should be for

mass. The magnitude is fairly large, as you would expect because this amount of octane is supposed to provide the energy for an entire city.

FOR PRACTICE 9.13 Chemical hand warmers popular with skiers and snowboarders produce heat when they are removed from their airtight plastic wrappers. They utilize the oxidation of iron to form iron(III) oxide according to the reaction: $4~{
m Fe}\,(s)+3~{
m O}_2\,(g) o 2~{
m Fe}_2{
m O}_3\,(s)$ Calculate $\Delta H_{
m rxn}^{^\circ}$ for this reaction and calculate how much heat is produced from a hand warmer containing 15.0 g of iron powder.

