
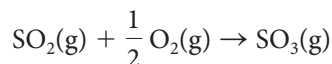


Standard Enthalpies of Formation

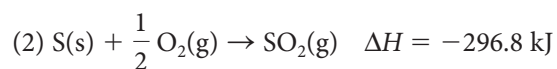
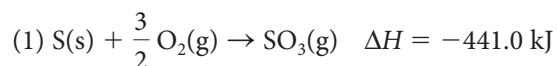
5.5

Sulfur dioxide gas, $\text{SO}_2(\text{g})$, is a colourless, odourless air pollutant. The majority of atmospheric sulfur dioxide gas comes from the combustion of fossil fuels containing sulfur impurities, such as those produced in coal-burning power plants (Figure 1). Once in the atmosphere, sulfur dioxide undergoes further chemical reactions to form acid precipitation, which can cause significant damage to aquatic ecosystems, in addition to having other negative effects on the environment.  CAREER LINK

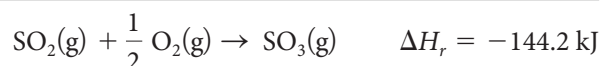
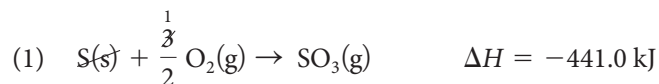
An important step in the production of acid precipitation is the reaction of sulfur dioxide with oxygen to produce sulfur trioxide. The balanced chemical equation for the formation of 1 mol of sulfur trioxide gas is



Measuring the enthalpy change of this reaction in the laboratory is difficult because the sulfur compounds are toxic. However, the enthalpy change can be calculated using Hess's law and the following thermochemical equations:



Applying Hess's law, equation (1) remains unchanged because sulfur trioxide gas is on the product side. Equation (2) is reversed so that sulfur dioxide gas is on the reactant side, resulting in equation (3).



Therefore, the enthalpy change for the production of sulfur trioxide gas is -144.2 kJ . Equations (1) and (2) are formation equations, and represent the formation of a compound from its elements.

Standard Enthalpy of Formation

The **standard enthalpy of formation** (ΔH_f°) of a compound is the change in enthalpy that occurs when 1 mol of a compound is formed from its elements, with all substances in their standard states. A substance is in a **standard state** when it is in its most stable form at SATP, (25°C , 100 kPa). Figure 2 shows oxygen, sodium, and mercury, each in their standard state.

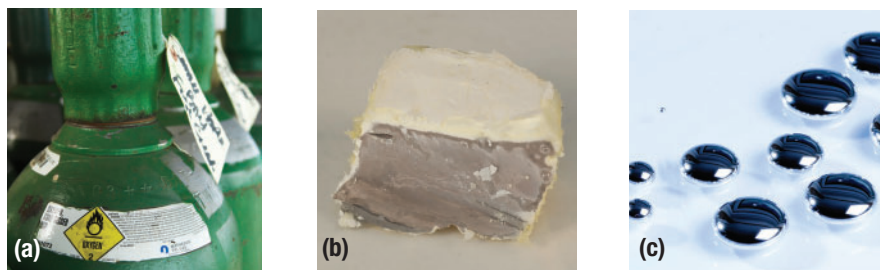


Figure 2 Three elements in their standard state: (a) oxygen gas, $\text{O}_2(\text{g})$; (b) sodium metal, $\text{Na}(\text{s})$; and (c) liquid mercury, $\text{Hg}(\text{l})$.

Most elements are solids in their standard state. However, the standard state of the noble gases, as well as of the diatomic elements—hydrogen, oxygen, nitrogen, fluorine, and chlorine—is the gas state. The standard state of bromine and mercury



Figure 1 Coal-burning power plants are a major artificial source of sulfur dioxide emissions.

standard enthalpy of formation (ΔH_f°) the change in enthalpy that accompanies the formation of 1 mol of a compound from its elements in their standard states

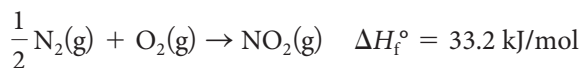
standard state the most stable form of a substance under standard conditions, 25°C and 100 kPa

Table 1 Standard Enthalpies of Formation for Several Compounds

Compound	ΔH_f° (kJ/mol)
AlCl ₃ (s)	-704.2
Al ₂ O ₃ (s)	-1675.7
CaSO ₄ (s)	-1434.1
Ca ₃ (PO ₄) ₂ (s)	-4120.8
CH ₃ OH(l)	-239.1
CH ₄ (g)	-74.4
C ₂ H ₂ (g)	+228.2
C ₂ H ₅ OH(l)	-235.2
C ₂ H ₆ (g)	-83.8
C ₃ H ₈ (g)	-104.7
C ₆ H ₁₂ O ₆ (s)	-1273.1
C ₈ H ₁₈ (l)	-250.1
C ₁₂ H ₂₂ O ₁₁ (s)	-2225.5
CO(g)	-110.5
CO ₂ (g)	-393.5
Fe ₂ O ₃ (s)	-824.2
HCN(g)	+135.1
HCl(g)	-92.3
HF(g)	-273.3
H ₂ O(g)	-241.8
H ₂ O(l)	-285.8
H ₂ SO ₄ (l)	-814.0
H ₃ PO ₄ (l)	-1271.7
MgO(s)	-601.6
Mg(OH) ₂ (s)	-924.5
NH ₃ (g)	-45.9
NH ₄ Cl(s)	-314.4
NH ₄ ClO ₄ (s)	-295.8
NO(g)	+90.2
NO ₂ (g)	+33.2
SiCl ₄ (l)	-687.0
SiO ₂ (s)	-910.7

is the liquid state. The standard state for a substance in solution is at a concentration of 1 mol/L. The degree sign on the symbol ΔH_f° indicates that the process takes place under standard conditions (25 °C, 100 kPa). The standard enthalpy of formation, ΔH_f° , of an element in its standard state is zero. A value of zero is assigned since an element is in its most fundamental form at standard conditions. Thus, the standard enthalpies of formation of oxygen gas, solid sodium metal, and liquid mercury metal, for example, are zero.

Consider the thermochemical equation for the formation of nitrogen dioxide gas from its elements in their standard states:



Like all standard enthalpy of formation equations, this standard enthalpy of formation equation shows the formation of 1 mol of the product. The formation of nitrogen dioxide gas from its elements is endothermic, absorbing 33.2 kJ/mol from its surroundings. Enthalpies of formation may be either exothermic or endothermic (**Table 1**).

Using Standard Enthalpies of Formation to Calculate Enthalpy Change

Since references such as Table 1 (left) provide the standard enthalpies of formation, ΔH_f° , for many pure substances, you can use these values to calculate the standard enthalpy of reaction, ΔH_r° , for many chemical reactions. Consider the combustion of methane gas, CH₄(g), represented by the balanced equation.

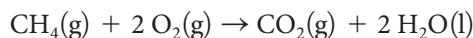


Figure 3 illustrates one possible pathway for the combustion of methane.

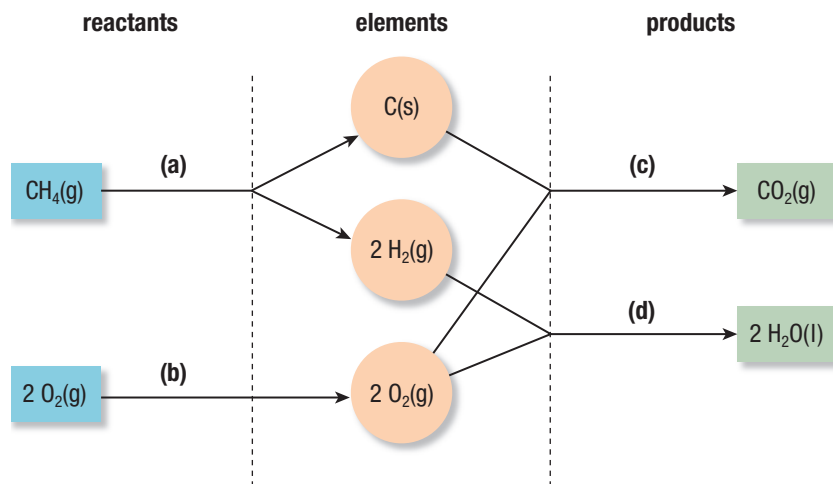
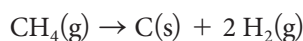


Figure 3 In this pathway for the combustion of methane, the reactants are broken down into their constituent elements in reactions (a) and (b). The elements are then used to synthesize the products in reactions (c) and (d).

In reactions (a) and (b) of the pathway shown in Figure 3, the reactants are decomposed into their elements. In reaction (a), methane is broken down into elemental carbon and hydrogen gas. The balanced chemical equation for the reaction is

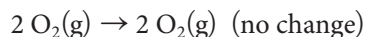


The equation above is the reverse of the formation equation for methane

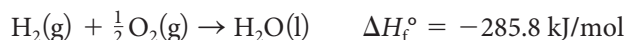


From Table 1 (left), you know that ΔH_f° for the formation of methane is -74.4 kJ/mol. Since you change the sign of ΔH whenever you reverse a reaction, ΔH° for the decomposition of methane into its elements is +74.4 kJ.

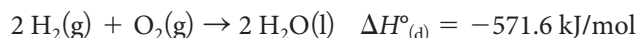
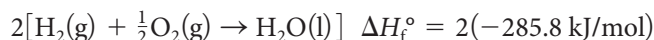
Oxygen gas exists in its elemental state, $O_2(g)$. It cannot be broken down further; no energy change occurs, so ΔH_f° is 0 kJ:



In reactions (c) and (d) of the pathway shown in Figure 3, the elements from the decomposition of the reactants combine to form the final products, $CO_2(g)$ and $H_2O(l)$. The balanced chemical equations are



Since 2 mol of water is formed in the combustion of methane, the ΔH_f° of $H_2O(l)$ must be multiplied by 2, as follows:



The change in enthalpy for the reaction is the sum of the ΔH° values:

$$\Delta H_r^\circ = 74.4 \text{ kJ} + 0 \text{ kJ} + (-393.5 \text{ kJ}) + (-571.6 \text{ kJ})$$

$$\Delta H_r^\circ = -890.7 \text{ kJ}$$

The use of ΔH_f° values to determine the enthalpy of combustion of methane is summarized in **Figure 4**. The decomposition of methane gas into its elements is an endothermic reaction; however, when elements combine to form products, a large quantity of energy is released.

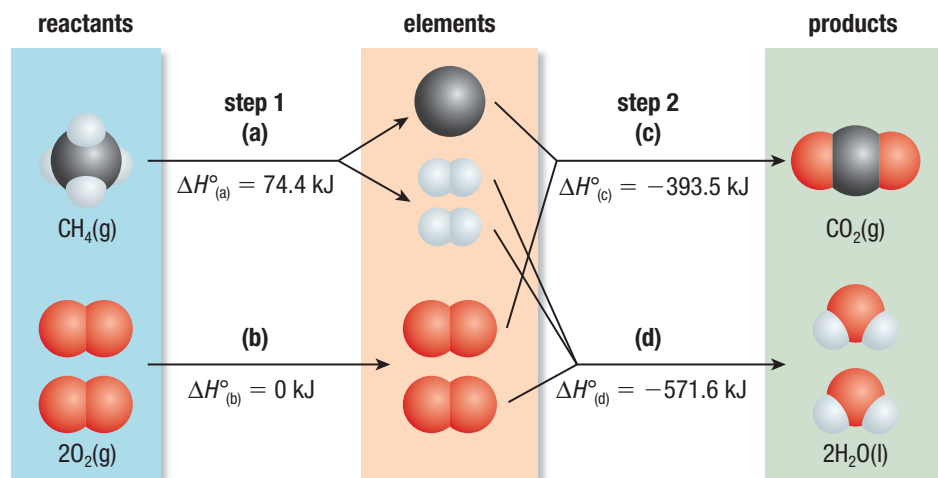


Figure 4 A schematic diagram of the energy changes for the reaction represented by the equation $CH_4(g) + 2 O_2(g) \rightarrow CO_2(g) + 2 H_2O(l)$

Since only ΔH_f° values were used in this example, we can state the following simplification: the enthalpy change for any reaction can be calculated by subtracting the sum of the enthalpies of formation of the reactants from the sum of the enthalpies of formation of the products. The enthalpies of formation are multiplied, as dictated by the balanced equation. That is,

$$\Delta H_r^\circ = \sum n_{\text{products}} \Delta H_{\text{products}}^\circ - \sum n_{\text{reactants}} \Delta H_{\text{reactants}}^\circ$$

where Σ represents the sum of terms, and n_{products} and $n_{\text{reactants}}$ represent the amount in moles of each product or reactant, respectively.

Investigation 5.5.1

Calorimetry versus Enthalpies of Formation (page 335)

Now that you have learned how standard enthalpies of formation are used to estimate the enthalpy change of a reaction, you will compare experimental results from calorimetry to enthalpies of formation.

Using this equation, the change in enthalpy for the combustion of methane gas is -890.7 kJ, which agrees with the value we obtained previously:

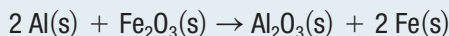
$$\begin{aligned}\Delta H_r^\circ &= [\Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}] - [\Delta H^\circ_{(a)} + \Delta H^\circ_{(b)}] \\ &= [-393.5 \text{ kJ} + 2(-285.8 \text{ kJ})] - (-74.4 \text{ kJ} + 0 \text{ kJ}) \\ &= -965.1 \text{ kJ} + 74.4 \text{ kJ} \\ \Delta H_r^\circ &= -890.7 \text{ kJ}\end{aligned}$$

Tutorial 1 ΔH and Standard Enthalpies of Formation

In this tutorial, you will calculate the enthalpy change of a reaction, ΔH , using standard enthalpy of formation values and Table 1 (page 320).

Sample Problem 1: Calculating ΔH from Standard Enthalpies of Formation

Using standard enthalpies of formation in Table 1, calculate the standard change in enthalpy for the thermite reaction represented by the balanced equation



Given: from Table 1, $\Delta H_f^\circ \text{ Fe}_2\text{O}_3\text{(s)} = -824.2$ kJ/mol; $\Delta H_f^\circ \text{ Al}_2\text{O}_3\text{(s)} = -1675.7$ kJ/mol;
 $\Delta H_f^\circ \text{ Al(s)} = 0$ kJ/mol; $\Delta H_f^\circ \text{ Fe(s)} = 0$ kJ/mol

Required: ΔH_r° for the thermite reaction

Analysis: $\Delta H_r^\circ = \sum n_{\text{products}} \Delta H_f^\circ \text{ products} - \sum n_{\text{reactants}} \Delta H_f^\circ \text{ reactants}$

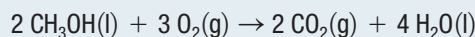
Solution: Since Fe(s) and Al(s) are in their standard states, you can rewrite this equation as

$$\begin{aligned}\Delta H_r^\circ &= n_{\text{Al}_2\text{O}_3\text{(s)}} \Delta H_f^\circ \text{ Al}_2\text{O}_3\text{(s)} - n_{\text{Fe}_2\text{O}_3\text{(s)}} \Delta H_f^\circ \text{ Fe}_2\text{O}_3\text{(s)} \\ &= -1675.7 \text{ kJ} - (-824.2 \text{ kJ}) \\ \Delta H_r^\circ &= -851.5 \text{ kJ}\end{aligned}$$

Statement: The standard enthalpy change for the thermite reaction is -851.5 kJ.

Sample Problem 2: Comparing Combustion Reactions

Until recently, liquid methanol was used to fuel high-performance engines in race cars. Gasoline is a mixture of hydrocarbons, but assume for this problem that gasoline is pure liquid octane, $\text{C}_8\text{H}_{18}\text{(l)}$. Using the data in Table 1, determine the standard enthalpy of combustion per gram of (a) methanol and (b) octane. Then (c) determine which fuel has the greater standard enthalpy per gram. The balanced chemical equation for the combustion of methanol is



The balanced chemical equation for the combustion of octane is



(a) **Given:** From Table 1: $\Delta H_f^\circ \text{ CH}_3\text{OH(l)} = -239.1$ kJ/mol; $\Delta H_f^\circ \text{ O}_2\text{(g)} = 0$ kJ/mol;
 $\Delta H_f^\circ \text{ CO}_2\text{(g)} = -393.5$ kJ/mol; $\Delta H_f^\circ \text{ H}_2\text{O(l)} = -285.8$ kJ/mol; $M_{\text{CH}_3\text{OH}} = 32.05$ g/mol

Required: ΔH° per gram CH_3OH for the combustion of methanol

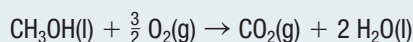
Analysis: $\Delta H_r^\circ = \sum n_{\text{products}} \Delta H_f^\circ \text{ products} - \sum n_{\text{reactants}} \Delta H_f^\circ \text{ reactants}$

Since $\text{O}_2\text{(g)}$ is in its standard state, you can write this equation as

$$\Delta H_r^\circ = [n_{\text{CO}_2\text{(g)}} \Delta H_f^\circ \text{ CO}_2\text{(g)} + n_{\text{H}_2\text{O(l)}} \Delta H_f^\circ \text{ H}_2\text{O(l)}] - n_{\text{CH}_3\text{OH(l)}} \Delta H_f^\circ \text{ CH}_3\text{OH(l)}$$

Solution:

Step 1. Rewrite the equation for the combustion of methanol so that methanol has a coefficient of 1:



Step 2. Insert the appropriate values into the equation for standard enthalpy of formation and solve:

$$\begin{aligned}\Delta H_r^\circ &= [n_{\text{CO}_2(\text{g})} \Delta H_f^\circ \text{CO}_2(\text{g}) + n_{\text{H}_2\text{O}(\text{l})} \Delta H_f^\circ \text{H}_2\text{O}(\text{l})] - n_{\text{CH}_3\text{OH}(\text{l})} \Delta H_f^\circ \text{CH}_3\text{OH}(\text{l}) \\ &= [-393.5 \text{ kJ} + 2(-285.8 \text{ kJ})] - (-239.1 \text{ kJ}) \\ &= -965.1 \text{ kJ} + 239.1 \text{ kJ} \\ \Delta H_r^\circ &= -726.0 \text{ kJ}\end{aligned}$$

Step 3. Convert to enthalpy per gram of liquid methanol:

$$\begin{aligned}\Delta H_{\text{per gram CH}_3\text{OH}}^\circ &= \left(\frac{-726.0 \text{ kJ}}{1 \text{ mol}}\right) \left(\frac{1 \text{ mol}}{32.05 \text{ g}}\right) \\ \Delta H_{\text{per gram CH}_3\text{OH}}^\circ &= -22.65 \text{ kJ}\end{aligned}$$

Statement: The combustion reaction of methanol releases 22.65 kJ/g methanol.

(b) **Given:** From Table 1: $\Delta H_f^\circ \text{C}_8\text{H}_{18}(\text{l}) = -250.1 \text{ kJ/mol}$; $\Delta H_f^\circ \text{O}_2(\text{g}) = 0 \text{ kJ/mol}$;
 $\Delta H_f^\circ \text{CO}_2(\text{g}) = -393.5 \text{ kJ/mol}$; $\Delta H_f^\circ \text{H}_2\text{O}(\text{l}) = -285.8 \text{ kJ/mol}$;
 $M_{\text{C}_8\text{H}_{18}} = 114.26 \text{ g/mol}$

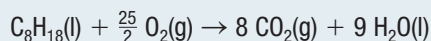
Required: $\Delta H_{\text{per gram C}_8\text{H}_{18}}^\circ$ for the combustion of octane

Analysis:

$$\Delta H_r^\circ = [n_{\text{CO}_2(\text{g})} \Delta H_f^\circ \text{CO}_2(\text{g}) + n_{\text{H}_2\text{O}(\text{l})} \Delta H_f^\circ \text{H}_2\text{O}(\text{l})] - n_{\text{C}_8\text{H}_{18}(\text{l})} \Delta H_f^\circ \text{C}_8\text{H}_{18}(\text{l})$$

Solution:

Step 1. Rewrite the equation for the combustion of octane so that octane has a coefficient of 1:



Step 2. Insert the appropriate values into the equation for standard enthalpy of formation and solve:

$$\begin{aligned}\Delta H_r^\circ &= [n_{\text{CO}_2(\text{g})} \Delta H_f^\circ \text{CO}_2(\text{g}) + n_{\text{H}_2\text{O}(\text{l})} \Delta H_f^\circ \text{H}_2\text{O}(\text{l})] - n_{\text{C}_8\text{H}_{18}(\text{l})} \Delta H_f^\circ \text{C}_8\text{H}_{18}(\text{l}) \\ &= [8(-393.5 \text{ kJ}) + 9(-285.8 \text{ kJ})] - (-250.1 \text{ kJ}) \\ &= (-3148 \text{ kJ} - 2572.2 \text{ kJ}) + 250.1 \text{ kJ} \\ \Delta H_r^\circ &= -5470.1 \text{ kJ/mol} \text{ or } -5.4701 \times 10^3 \text{ kJ/mol}\end{aligned}$$

Step 3. Convert to enthalpy per gram of C_8H_{18} :

$$\begin{aligned}\Delta H_{\text{per gram C}_8\text{H}_{18}}^\circ &= \left(\frac{-5.4701 \times 10^3 \text{ kJ}}{1 \text{ mol}}\right) \left(\frac{1 \text{ mol}}{114.22 \text{ g/mol}}\right) \\ \Delta H_{\text{per gram C}_8\text{H}_{18}}^\circ &= -47.891 \text{ kJ/g}\end{aligned}$$

Statement: The combustion reaction of octane releases -47.891 kJ of energy per gram of octane.

(c) **Solution:** The enthalpy of combustion per gram of octane is more than twice that per gram of methanol.

Practice

- Calculate the enthalpy of combustion for acetylene gas, $\text{C}_2\text{H}_2(\text{g})$, using standard enthalpies of formation values. T/1 [ans: -1301.0 kJ/mol]
- Compare the enthalpy of combustion for 1.00 g of acetylene gas to that of 1.00 g of propane gas, $\text{C}_3\text{H}_8(\text{g})$, using standard enthalpies of formation values. T/1
 [ans: $\Delta H_c^\circ \text{acetylene} = -50.0 \text{ kJ/g}$, $\Delta H_c^\circ \text{propane} = -50.3 \text{ kJ/g}$]

5.5 Review

Summary

- The standard enthalpy of formation, ΔH_f° , of a compound is the change in enthalpy that accompanies the formation of 1 mol of a compound from its elements, with all elements in their standard states.
- The standard state of an element is the state of matter in which the element exists under SATP conditions (25 °C, 100 kPa).
- The enthalpy of formation of any element in its standard state is equal to zero.
- The enthalpy change for a reaction is determined by subtracting the enthalpies of formation of the reactants from the enthalpies of formation of the products:

$$\Delta H_{\text{reaction}}^\circ = \sum n_{\text{products}} \Delta H_{\text{products}}^\circ - \sum n_{\text{reactants}} \Delta H_{\text{reactants}}^\circ$$

Questions

- Which of the following elements is in its standard state? [K/U](#) [T/I](#)
 - Hg(g)
 - Mg(s)
 - O₂(l)
 - Br₂(l)
- Calculate ΔH° for the reactions represented by the following equations: [K/U](#) [T/I](#)
 - 2 H₂(g) + O₂(g) → 2 H₂O(l)
 - C(s) + O₂(g) → CO₂(g)
 - 2 H₂O(l) → 2 H₂(g) + O₂(g)
 - C₂H₅OH(l) + 3 O₂(g) → 2 CO₂(g) + 3 H₂O(l)
- The combustion reaction of octane is represented by the equation
$$2 \text{C}_8\text{H}_{18}(\text{l}) + 25 \text{O}_2(\text{g}) \rightarrow 16 \text{CO}_2(\text{g}) + 18 \text{H}_2\text{O}(\text{l})$$
$$\Delta H_{\text{r}} = -1.09 \times 10^4 \text{ kJ}$$
What is the ΔH° for the reaction given by the following equation?
$$8 \text{CO}_2(\text{g}) + 9 \text{H}_2\text{O}(\text{l}) \rightarrow \text{C}_8\text{H}_{18}(\text{l}) + \frac{25}{2} \text{O}_2(\text{g})$$
 [K/U](#) [T/I](#)
- The fuel used in reusable booster rockets consists of a mixture of aluminum and ammonium perchlorate. The following equation represents a possible reaction of this mixture:
$$3 \text{Al}(\text{s}) + 3 \text{NH}_4\text{ClO}_4(\text{s}) \rightarrow \text{Al}_2\text{O}_3(\text{s}) + \text{AlCl}_3(\text{s}) + 3 \text{NO}(\text{g}) + 6 \text{H}_2\text{O}(\text{g})$$
Using enthalpies of formation, calculate ΔH° for this reaction. [K/U](#) [T/I](#)
- Consider the reaction between chlorine trifluoride gas, ClF₃(g), and ammonia gas, NH₃(g), represented by the equation
$$2 \text{ClF}_3(\text{g}) + 2 \text{NH}_3(\text{g}) \rightarrow \text{N}_2(\text{g}) + 6 \text{HF}(\text{g}) + \text{Cl}_2(\text{g})$$
$$\Delta H^\circ = -1196 \text{ kJ}$$
Calculate ΔH_f° for ClF₃(g). [K/U](#) [T/I](#)
- The oxidation of methylhydrazine, N₂H₃CH₃(l), by dinitrogen tetroxide, N₂O₄(l), was used for propulsion in the Space Shuttle orbiter. This reaction is represented by the equation
$$4 \text{N}_2\text{H}_3\text{CH}_3(\text{l}) + 5 \text{N}_2\text{O}_4(\text{l}) \rightarrow 12 \text{H}_2\text{O}(\text{g}) + 9 \text{N}_2(\text{g}) + 4 \text{CO}_2(\text{g})$$
The enthalpy of formation for liquid methylhydrazine is +53 kJ/mol and the enthalpy of formation for liquid dinitrogen tetroxide is -20 kJ/mol. Calculate ΔH° for this reaction. [K/U](#) [T/I](#)
- The standard enthalpy of combustion of ethene gas, C₂H₄(g), is -1411.1 kJ/mol at SATP. Calculate ΔH_f° for ethene gas. [K/U](#) [T/I](#)
- Liquid ethanol, C₂H₅OH(l), has been proposed as an alternative fuel. Calculate the standard enthalpy of combustion per gram of liquid ethanol. [K/U](#) [T/I](#)
- Methanol, CH₃OH(l), has been proposed as an alternative fuel. [K/U](#) [T/I](#) [A](#)
 - Calculate the standard enthalpy of combustion per gram of liquid methanol.
 - Compare the standard enthalpy of combustion per gram of methanol to that of ethanol in Question 8.
 - Based on your answer in (b), which fuel would be the most convenient source of energy for a vehicle? Explain why.
- The melting point of the element gallium, Ga(s), is so low that gallium will melt in your hand. The quantity of thermal energy required to melt gallium is 5.59 kJ/mol. [K/U](#) [T/I](#)
 - Write a thermochemical equation for the melting of gallium.
 - What are the enthalpies of formation of solid and liquid gallium at SATP? Why are they not equal?