Ch 9 Energy, Enthalpy, and Thermochemistry
9.1 The nature of energy

*Energy*: the capacity to do work or to produce heat.

*Law of conservation of energy*: the energy can be converted from one form to another but can be neither created nor destroyed. That is, *the energy of the universe is constant*. 
Energy can be classified as either *potential energy* or *kinetic energy*.

*Potential energy* is due to position or composition. I.e., water behind a dam, attractive/repulsive forces…

*Kinetic energy* of an object is due to the motion & depends on the mass of the object (m) & its velocity (v) : \( KE = \frac{1}{2}m v^2 \).
Figure 9.1: Initial positions ball A has a higher potential energy than ball B.
From Figure 9.1:

1. Frictional heating

2. Work (ball A has done a work on B): defined as a force acting over a distance. Work is required to raise B from its original position to a higher one.

Thus, there are two ways to transfer energy: through work & through heat.
Regardless of the condition of the hill’s surface, the total energy transferred will be constant. The amounts of heat & work will differ. Energy change is independent of the pathway; however, work & heat are both dependent on the pathway.
A state function (property) refers to a property of the system that depends only on its present state.

A state function (property) is that a change in this function (property) in going from one state to another is independent of the particular pathway taken between the two states.

Energy is a state function, but work & heat are not state functions.
Chemical energy:

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(g) + \text{energy (heat)} \]

The *universe* can be divided into two parts: *the system (reactants/products of the reaction)* & *surroundings (everything else)*.
When a reaction results in the evolution of heat, it is said to be *exothermic*.

Reactions that absorb energy from the surroundings are said to be *endothermic*.

*The energy gained by the surroundings must be equal to the energy lost by the system.*
In combustion of methane (CH$_4$), the heat flow into the surroundings results in a lowering of the potential energy of the reaction system (*this always holds true*).

In any exothermic reaction, the potential energy stored in the chemical bonds is being converted to thermal energy (random kinetic energy) via heat.
Figure 9.2: Combustion of methane releases the quantity of energy.
Figure 9.3: Energy diagram for the reaction of nitrogen and oxygen

- System:
  - 1 mol N₂
  - 1 mol O₂
  - 2 mol NO (Products)

- Surroundings:
  - Heat absorbed from the surroundings

\[ \Delta(PE) \]
The study of energy & its interconversion is called **thermodynamics**. *The law of conservation of energy* is often called the **first law of thermodynamics** & is stated as:

*the energy of the universe is constant.*
Internal energy \((E)\) is defined as the sum of the kinetic & potential energies of all the “particles” in the system.

\[ \Delta E = q + w; \quad q : \text{heat}, \ w : \text{work} \]

The meaning of a number (magnitude of the change) & a sign (the direction of the flow & this reflects the system’s point of view) should be remembered.
Interconversion between system & surroundings for energy

\[ \Delta E < 0 \quad \text{System} \]

\[ \Delta E > 0 \quad \text{System} \]
Figure 9.4: The piston moving a distance

\[ P = \frac{F}{A} \]

(a) Initial state  (b) Final state

Area = A

\[ \Delta V \]

\[ \Delta h \]
Work is defined as a force applied over a given distance, so if the piston moves a distance $\Delta h$, as shown in Fig. 9.4, then the magnitude of the work is:

$$|\text{Work}| = |\text{force \times distance}| = |F \times \Delta h|$$

Since $P = F/A$, or $F = P \times A$, then

$$|\text{Work}| = |F \times \Delta h| = |P \times A \times \Delta h|$$

$$\Delta V = \text{final volume} - \text{initial volume} = A \times \Delta h$$

Substituting $\Delta V = A \times \Delta h$ into the expression for the magnitude of the work gives

$$|\text{Work}| = |P \times A \times \Delta h| = |P \Delta V|$$
Expanded: \( w = -p\Delta V (<0) \)
Compressed: \( w = -p\Delta V (>0) \)

In dealing with “PV work” keep in mind that the P in \( P\Delta V \) always refers to the external pressure - the pressure that causes a compression or that resists an expansion.
Example 9.1

A balloon is inflated to its full extent by heating the air inside it. In the final stages of this process the volume of the balloon changes from $4.00 \times 10^6$ L to $4.50 \times 10^6$ L by addition of $1.3 \times 10^8$ J of energy as heat. Assuming the balloon expands against a constant pressure of 1.0 atm, calculate $\Delta E$ for the process.

**Solution**

To calculate $\Delta E$ we use the equation

$$\Delta E = q + w$$

Since the problem states that $1.3 \times 10^8$ J of energy is added as heat,

$$q = +1.3 \times 10^8 \text{ J}$$

The work done can be calculated from the expression

$$w = -P\Delta V$$
In this case $P = 1.0$ atm (the external pressure) and

$$\Delta V = V_{\text{final}} - V_{\text{initial}}$$

$$= 4.50 \times 10^6 \text{ L} - 4.00 \times 10^6 \text{ L} = 0.50 \times 10^6 \text{ L}$$

$$= 5.0 \times 10^5 \text{ L}.$$  \[ R = 0.08206 \text{ Latm/Kmol} \]
\[ = 8.3145 \text{ J/Kmol} \]

Thus

$$w = -1.0 \text{ atm} \times 5.0 \times 10^5 \text{ L} = -5.0 \times 10^5 \text{ L atm}$$

$$w = -5.0 \times 10^5 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = -5.1 \times 10^7 \text{ J}$$

Then

$$\Delta E = q + w = (+1.3 \times 10^8 \text{ J}) + (-5.1 \times 10^7 \text{ J}) = 8 \times 10^7 \text{ J}$$

$< 0$
9.2 Enthalpy ($\text{焓}$)

$$H = E + PV$$

$H$ : enthalpy, $E$ : internal energy
$P$, $V$ : properties of the system
$H$, $E$, $P$, & $V$ are all state functions.
**What is exactly enthalpy (H) ?**

Consider a process carried out at constant pressure:

\[
\Delta E = q_p + w
\]

becomes

\[
\Delta E = q_p - P\Delta V
\]

or

\[
q_p = \Delta E + P\Delta V
\]

where \(q_p\) is the heat at constant pressure.

We will now relate \(q_p\) to the change in enthalpy. The definition of enthalpy is \(H = E + PV\). Therefore

\[
(\text{change in } H) = (\text{change in } E) + (\text{change in } PV)
\]

or

\[
\Delta H = \Delta E + \Delta(PV)
\]
Since $P$ is constant, the change in $PV$ is caused only by a change in volume. Thus

$$\Delta(PV) = P\Delta V$$

and

$$\Delta H = \Delta E + P\Delta V$$

This expression is identical to the one we obtained for $q_P$:

$$q_P = \Delta E + P\Delta V$$

Thus, for a process carried out at constant pressure,

$$\Delta H = q_P.$$
At constant pressure (where only PV work is allowed) the change in enthalpy ($\Delta H$) of the system is equal to the energy flow as heat ($q_P$) from the above.

$$\Delta H = H_{\text{products}} - H_{\text{reactants}}$$ (for a chemical reaction the enthalpy change)

$\Delta H > 0$ – endothermic; $\Delta H < 0$ – exothermic.
9.3 Thermodynamics of ideal gases

Ideal gases: the high temp & low pressure for real gases \((PV = nRT)\).

\((KE)_{avg} = \frac{3}{2} RT\) (Ch. 5 for an ideal gas) represents average, random, translational energy for 1 mole of gas at a given temp. Energy ("heat") required \(= \frac{3}{2} R\Delta T\).
The *molar heat capacity* of a substance is defined as the energy required to raise the temp. of 1 mole of that substance by 1 K. Thus, the *molar heat capacity* of an ideal gas is $3/2 \, R$. 
Heating an ideal gas at constant volume

$C_V = \frac{3}{2} R = \text{“heat” required to change the temp of 1 mole of gas by 1 K at constant volume (}$\Delta V=0$, no PV work & all the energy that flows into the gas is used to increase the translational energies of the gas molecules).
Heating an ideal gas at constant pressure

In this case, its volume increases & PV work occurs.

Energy required = “heat”
= energy needed to change the translational energy
+ energy needed to do the PV work
The quantity of work done as the gas expanded by $\Delta V$ is $P\Delta V$.

$$ P\Delta V = nR\Delta T = R\Delta T $$

Thus for a 1K change ($\Delta T=1K$) the work is $R$, & heat required to increase the temp of 1 mole of gas by 1 K (constant $P$) = $3/2 \ R \ (C_V) + R = 5/2 \ R = C_V + R = C_P$
**Heating a polyatomic gas**: as a polyatomic gas is heated, the gas molecules absorb energy to increase their rotational & vibrational motions as well as to move through space (translate) at higher speeds. (previous discussion: the temperature of a mono-atomic ideal gas is an index of the average random translational energy of the gas).
Indeed, when a gas is heated, the temperature only increases to the extent that the translational energies of the molecules increase. Any energy that is absorbed to increase the vibrational & rotational energies does not contribute directly to the translational kinetic energy. Thus, its heat capacity is larger than $3/2 \ R$. But, finally the $C_P - C_V = R$ is also applicable in all cases, as expected for gases that closely obey the ideal gas law.
### Table 9.1: Molar Heat Capacities of Various Gases at 298 K

<table>
<thead>
<tr>
<th>Gas</th>
<th>$C_v \left( \frac{J}{K \text{ mol}} \right)$</th>
<th>$C_p \left( \frac{J}{K \text{ mol}} \right)$</th>
<th>$C_p - C_v$</th>
</tr>
</thead>
<tbody>
<tr>
<td>He, Ne, Ar</td>
<td>12.47</td>
<td>20.80</td>
<td>8.33</td>
</tr>
<tr>
<td>H$_2$</td>
<td>20.54</td>
<td>28.86</td>
<td>8.32</td>
</tr>
<tr>
<td>N$_2$</td>
<td>20.71</td>
<td>29.03</td>
<td>8.32</td>
</tr>
<tr>
<td>N$_2$O</td>
<td>30.38</td>
<td>38.70</td>
<td>8.32</td>
</tr>
<tr>
<td>CO$_2$</td>
<td>28.95</td>
<td>37.27</td>
<td>8.32</td>
</tr>
<tr>
<td>C$_2$H$_6$</td>
<td>44.60</td>
<td>52.92</td>
<td>8.32</td>
</tr>
</tbody>
</table>

**CO$_2$ v.s. N$_2$**

$R=8.3145 \text{ J/Kmol}$
Heating a gas: energy and enthalpy

E = \frac{3}{2} RT \text{ (per mole)} \text{ (the average translational energy of an ideal gas - a monoatomic ideal gas)}

The energy (temp dependence) of an ideal gas:

\Delta E = \frac{3}{2} R \Delta T \text{ (per mole)}

Note that this expression corresponds to:

\Delta E = C_v \Delta T \text{ (per mole)} \text{ or } \Delta E = nC_v \Delta T \text{ (n moles)}
The $C_V$ appears because \textit{when a gas is heated at constant volume, all the input energy (heat) goes toward increasing $E$ (no heat is needed to do work)}. 
On the other hand, when a gas is heated at constant pressure, the volume changes & work occurs:

"heat" required = \( q_P = nC_p \Delta T = n(C_V + R) \Delta T \)

\( = nC_V \Delta T + nR \Delta T \)

- \( \Delta E \)
- \( P \Delta V \) = work required

(E for an ideal gas depends only on T)
Consider the change in enthalpy when a gas is heated

\[ H = E + PV \]

\[ \Delta H = \Delta E + \Delta(PV) = \Delta E + \Delta(nRT) \]

\[ = \Delta E + nR\Delta T \]

For a sample of ideal gas containing \( n \) moles, substituting \( \Delta E = nC_V\Delta T \)

\[ \Delta H = nC_V\Delta T + nR\Delta T = n(C_V + R)\Delta T \]

\[ = nC_P\Delta T \quad (C_P = C_V + R) \]
Thus, we can use $\Delta H = nC_p\Delta T$ to calculate the change in enthalpy when $n$ moles of an ideal gas is heated, regardless of any conditions on pressure or volume.

$E \propto T \ (E = \frac{3}{2}RT)$; $H \propto T \ (PV = nRT)$

Proportional constant $C_V$  Proportional constant $C_p$
Table 9.2: Thermodynamic properties of an ideal gas

<table>
<thead>
<tr>
<th>Expression</th>
<th>Application</th>
</tr>
</thead>
<tbody>
<tr>
<td>( C_v = \frac{3}{2}R )</td>
<td>Monatomic ideal gas</td>
</tr>
<tr>
<td>( C_v &gt; \frac{3}{2}R )</td>
<td>Polyatomic ideal gas (value must be measured</td>
</tr>
<tr>
<td></td>
<td>experimentally)</td>
</tr>
<tr>
<td>( C_p = C_v + R )</td>
<td>All ideal gases</td>
</tr>
<tr>
<td>( C_p = \frac{5}{2}R = \frac{3}{2}R + R )</td>
<td>Monatomic ideal gas</td>
</tr>
<tr>
<td>( C_p &gt; \frac{5}{2}R )</td>
<td>Polyatomic ideal gas (specific value depends on</td>
</tr>
<tr>
<td></td>
<td>the value of ( C_v ))</td>
</tr>
<tr>
<td>( \Delta E = nC_v \Delta T )</td>
<td>All ideal gases</td>
</tr>
<tr>
<td>( \Delta H = nC_p \Delta T )</td>
<td>All ideal gases</td>
</tr>
</tbody>
</table>
Example 9.2

Consider 2.00 mol of a monatomic ideal gas that is taken from state A \( (P_A = 2.00 \text{ atm}, \ V_A = 10.0 \text{ L}) \) to state B \( (P_B = 1.00 \text{ atm}, \ V_B = 30.0 \text{ L}) \) by two different pathways:

\[
\begin{align*}
1 & : (V_C = 30.0 \text{ L} \\
   & \quad P_C = 2.00 \text{ atm}) \\
3 & : (V_D = 10.0 \text{ L} \\
   & \quad P_D = 1.00 \text{ atm})
\end{align*}
\]

State A \( (V_A = 10.0 \text{ L} \)
\( (P_A = 2.00 \text{ atm}) \)

State B \( (V_B = 30.0 \text{ L} \)
\( (P_B = 1.00 \text{ atm}) \)

Calculate \( q, w, \Delta E, \) and \( \Delta H \) for both pathways.
Figure 9.5: Summary of the two pathways discussed in example 9.2.
**Step 1 (constant P)**

Notice from Fig. 9.5 that this step corresponds to an expansion from 10.0 to 30.0 L at a constant pressure of 2.00 atm. This process must occur by heating the gas to produce some temperature change $\Delta T$ (not specified in the given data). From the ideal gas law we know that

$$P\Delta V = nR\Delta T$$

In this case $\Delta V = 30.0 \text{ L} - 10.0 \text{ L}$, so

$$P\Delta V = (2.00 \text{ atm})(20.0 \text{ L}) = 4.00 \times 10^1 \text{ L atm}$$

or if we convert to joules,

$$P\Delta V = 4.00 \times 10^1 \text{ L atm} \times \frac{101.3 \text{ J}}{\text{L atm}} = 4.05 \times 10^3 \text{ J}$$
\[ \Delta T = \frac{P \Delta V}{nR} = \frac{4.05 \times 10^3 \text{ J}}{nR} \]

We know that \( w = -P \Delta V \), and because in this case the gas expands against a constant external pressure of 2.00 atm, we have

\[ w_1 = -(2.00 \text{ atm})(30.0 \text{ L} - 10.0 \text{ L}) = -4.00 \times 10^1 \text{ L atm} \]

\[ = -4.05 \times 10^3 \text{ J} \]

\[ \Delta H = nC_p \Delta T = q_p \]

Also, in this case (constant \( P \))

\[ q_1 = q_p = nC_p \Delta T \]

\[ = n \left( \frac{5}{2} R \right) \left( \frac{4.05 \times 10^3 \text{ J}}{nR} \right) = 1.01 \times 10^4 \text{ J} \]

(Note that the signs of \( w \) and \( q \) are as expected: The gas expands, so flows out of the system; the gas is heated, so heat flows into the system.)

We can calculate \( \Delta E_1 \) and \( \Delta H_1 \) as follows:

\[ \Delta E_1 = nC_v \Delta T = n \left( \frac{3}{2} R \right) \left( \frac{4.05 \times 10^3 \text{ J}}{nR} \right) = 6.08 \times 10^3 \text{ J} \]

\[ \Delta H_1 = nC_p \Delta T = n \left( \frac{5}{2} R \right) \left( \frac{4.05 \times 10^3 \text{ J}}{nR} \right) = 1.01 \times 10^4 \text{ J} \]
Step 2 (constant V)

In this step the gas pressure decreases from 2.00 atm to 1.00 atm at constant volume. This step must correspond to the cooling of the gas by a quantity $\Delta T$, which we can find from the ideal gas law:

$$\Delta PV = nR\Delta T$$

$$\Delta T = \frac{\Delta PV}{nR} = \frac{(1.00 \text{ atm} - 2.00 \text{ atm})(30.0 \text{ L})}{nR}$$

$$= \frac{-30.0 \text{ L atm}}{nR} = \frac{-3.04 \times 10^3 \text{ J}}{nR}$$

Note that $\Delta T$ is negative, as expected for a cooling process. Because in this step $\Delta V = 0$, thus $\omega_2 = 0$. In this case

$$q_2 = q_v = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^3 \text{ J}}{nR}\right)$$

$$= -4.56 \times 10^3 \text{ J}$$

$$\Delta E_2 = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-3.04 \times 10^3 \text{ J}}{nR}\right)$$

$$= -4.56 \times 10^3 \text{ J} = q_v$$

$$\Delta H_2 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-3.04 \times 10^3 \text{ J}}{nR}\right)$$

$$= -7.60 \times 10^3 \text{ J}$$
Step 3 (constant V)

\[ \Delta T = \frac{\Delta PV}{nR} = \frac{(-1.00 \text{ atm})(10.0 \text{ L})}{nR} = \frac{-10.0 \text{ L atm}}{nR} \]

\[ = \frac{-1.01 \times 10^3 \text{ J}}{nR} \]

\[ \omega_3 = 0 \quad (\Delta V = 0) \]

\[ q_3 = q_v = nC_v\Delta T = n\left(\frac{3}{2}R\right)\left(\frac{-1.01 \times 10^3 \text{ J}}{nR}\right) \]

\[ = -1.52 \times 10^3 \text{ J} \]

\[ \Delta E_3 = q_v = -1.52 \times 10^3 \text{ J} \]

\[ \Delta H_3 = nC_p\Delta T = n\left(\frac{5}{2}R\right)\left(\frac{-1.01 \times 10^3 \text{ J}}{nR}\right) = -2.53 \times 10^3 \text{ J} \]
Step 4  \textbf{(constant P)}

\[ \Delta T = \frac{P \Delta V}{nR} = \frac{(1.00 \text{ atm})(20.0 \text{ L})}{nR} = \frac{20.0 \text{ L atm}}{nR} \]

\[ = \frac{2.03 \times 10^3 \text{ J}}{nR} \]

\[ w_4 = -P \Delta V = -(1.00 \text{ atm})(20.0 \text{ L}) = -20.0 \text{ L atm} \]

\[ = -2.03 \times 10^3 \text{ J} \]

\[ q_4 = q_p = nC_p \Delta T = n \left( \frac{5}{2} R \right) \left( \frac{2.03 \times 10^3 \text{ J}}{nR} \right) \]

\[ = 5.08 \times 10^3 \text{ J} \]

\[ \Delta E_4 = nC_v \Delta T = n \left( \frac{3}{2} R \right) \left( \frac{2.03 \times 10^3 \text{ J}}{nR} \right) \]

\[ = 3.05 \times 10^3 \text{ J} \]

\[ \Delta H_4 = nC_p \Delta T = n \left( \frac{5}{2} R \right) \left( \frac{2.03 \times 10^3 \text{ J}}{nR} \right) \]

\[ = 5.08 \times 10^3 \text{ J} = q_p \]
Summary

- Pathway one (steps 1 and 2):

\[
q_{\text{one}} = q_1 + q_2 = 1.01 \times 10^4 \text{ J} - 4.56 \times 10^3 \text{ J}
= 5.5 \times 10^3 \text{ J}
\]

\[
w_{\text{one}} = w_1 + w_2 = -4.05 \times 10^3 \text{ J}
\]

\[
q_{\text{one}} + w_{\text{one}} = 1.5 \times 10^3 \text{ J} = \Delta E_{\text{one}}
\]

\[
\Delta H_{\text{one}} = \Delta H_1 + \Delta H_2
= 1.01 \times 10^4 \text{ J} - 7.60 \times 10^3 \text{ J}
= 2.5 \times 10^3 \text{ J}
\]
• Pathway two (steps 3 and 4):

\[ q_{two} = q_3 + q_4 = -1.52 \times 10^3 \text{ J} + 5.08 \times 10^3 \text{ J} = 3.56 \times 10^3 \text{ J} \]

\[ w_{two} = w_3 + w_4 = -2.03 \times 10^3 \text{ J} \]

\[ q_{two} + w_{two} = 3.55 \times 10^3 \text{ J} - 2.03 \times 10^3 \text{ J} = 1.52 \times 10^3 \text{ J} = \Delta E_{two} \]

\[ \Delta H_{two} = \Delta H_3 + \Delta H_4 \]

\[ = -2.53 \times 10^3 \text{ J} + 5.08 \times 10^3 \text{ J} = 2.55 \times 10^3 \text{ J} \]

\[ \Delta E_1 = \Delta E_2 \& \Delta H_1 = \Delta H_2 \]
Figure 9.6: Magnitude of the work for pathway (a) and (b) is shown by the colored areas: $|w| = |P\Delta V|$.

$\Delta E = q + w$; $q$, $w$ : related to the pathway

$E$ is a state function.
9.4 Calorimetry

Calorimeter: a device to determine the heat associated with a chemical reaction experimentally (temp change & energy absorbed).

\[ C \text{ (heat capacity)} = \text{heat absorbed/increase in temp} \]
**Specific heat capacity** (JK$^{-1}$g$^{-1}$ or J°C$^{-1}$g$^{-1}$) : the energy required to raise the temp of 1 g of a substance by 1 °C.

**Molar heat capacity** (JK$^{-1}$mol$^{-1}$ or J°C$^{-1}$mol$^{-1}$) : the energy required to raise the temp of 1 mol of a substance by 1 °C.
Figure 9.7: Coffee cup calorimeter made of two Styrofoam cups
### TABLE 9.3  The Specific Heat Capacities of Some Common Substances

<table>
<thead>
<tr>
<th>Substance</th>
<th>Specific Heat Capacity (J °C⁻¹ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂O(l)</td>
<td>4.18</td>
</tr>
<tr>
<td>H₂O(s)</td>
<td>2.03</td>
</tr>
<tr>
<td>Al(s)</td>
<td>0.89</td>
</tr>
<tr>
<td>Fe(s)</td>
<td>0.45</td>
</tr>
<tr>
<td>Hg(l)</td>
<td>0.14</td>
</tr>
<tr>
<td>C(s) (graphite)</td>
<td>0.71</td>
</tr>
</tbody>
</table>
For example, suppose we mix 50.0 mL of 1.0 M HCl with 50.0 mL of 1.0 M NaOH at 25°C in a calorimeter.

\[ H^+_{(aq)} + OH^-_{(aq)} \rightarrow H_2O_{(l)} \]

Energy released by reaction
= energy absorbed by the solution
= specific heat capacity x mass of solution x \( \Delta T \),

where \( \Delta T = 31.9°C \rightarrow 25.0° = 6.9 \ °C \)
Mass of solution = 100.0 mL x 1.0 g/mL = 1.0 x 10^2 g
Energy released = (4.18 J/°C g)(1.0 x 10^2 g)(6.9°C)
               = 2.9 x 10^3 J
2.9 x 10^3 / 5.0 x 10^{-2} mol (mol of H^+) = 5.8 x 10^4 J
ΔH = -58 KJ/mol
Example 9.3

When 1.00 L of 1.00 M Ba(NO₃)₂ at 25.0°C is mixed with 1.00 L of 1.00 M Na₂SO₄ at 25°C in a calorimeter, the white solid BaSO₄ forms and the temperature of the mixture increases to 28.1°C. Assuming that the calorimeter absorbs only a negligible quantity of heat, that the specific heat capacity of the solution is 4.18 J °C⁻¹ g⁻¹, and that the density of the final solution is 1.0 g/mL, calculate the enthalpy change per mole of BaSO₄ formed.

**Solution**

\[ \text{Ba}^{2+}(aq) + \text{SO}_4^{2-}(aq) \rightarrow \text{BaSO}_4(s) \]
Since the temperature increases, the formation of solid \( \text{BaSO}_4 \) must be exothermic; \( \Delta H \) will be negative.

Heat evolved by reaction  = heat absorbed by solution

= specific heat capacity \( \times \) mass of solution
\( \times \) increase in temperature

Since 1.00 L of each solution is used, the total solution volume is 2.00 L, and

\[
\text{Mass of solution} = 2.00 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1.0 \text{ g}}{\text{mL}}
\]

\[
= 2.0 \times 10^3 \text{ g}
\]
Temperature increase  = 28.1°C − 25.0°C = 3.1°C

Heat evolved = (4.18 J °C⁻¹ g⁻¹)(2.0 × 10³ g)(3.1°C)
              = 2.6 × 10⁴ J

Thus  
q = q_p = ∆H = −2.6 × 10⁴ J

Since 1.00 L of 1.00 M Ba(NO₃)₂ contains 1 mol of Ba²⁺ ions, and 1.00 L of 1.00 M Na₂SO₄ contains 1.00 mol of SO₄²⁻ ions, 1.00 mol of solid BaSO₄ is formed in this experiment. Thus the enthalpy change per mole of BaSO₄ formed is

∆H = −2.6 × 10⁴ J/mol = −26 kJ/mol
Calculation of $\Delta H$ & $\Delta E$ for cases in which PV work occurs

(1) $\Delta E = q_{(P)} + W = \Delta H + 0$
(at constant pressure, where $\Delta V=0$, $W = 0$ & thus $\Delta E = \Delta H = q_P$ / solution reaction)

(2) $2\text{SO}_2(g) + \text{O}_2(g) \rightarrow 2\text{SO}_3(g)$ (gas reaction)

$\Delta H = q_P$ (at constant pressure)

$W = -P\Delta V$ ($\Delta V<0$) $\Delta E = q_P + W = \Delta H + W$

$\Delta E \neq \Delta H$
Figure 9.8: Schematic to show the change in volume for the reaction
Example 9.4

When 2.00 mol of $\text{SO}_2(g)$ reacts completely with 1.00 mol of $\text{O}_2(g)$ to form 2.00 mol of $\text{SO}_3(g)$ at 25°C and a constant pressure of 1.00 atm, 198 kJ of energy is released as heat. Calculate $\Delta H$ and $\Delta E$ for this process.

Solution

The value of $\Delta E$ can be calculated from the relationship

$$\Delta E = q + w$$
Since $q$ is known ($-198$ kJ), we only need the value for $w$. We know that:

$$w = -P\Delta V$$

Solving the ideal gas law for $\Delta V$ gives:

$$\Delta V = \Delta n\left(\frac{RT}{P}\right)$$

where only $n$ changes ($T$ and $P$ are constant) as the reaction occurs. In this case:

$$\Delta n = n_{\text{final}} - n_{\text{initial}}$$
So \( \Delta n = 2 \text{ mol} - 3 \text{ mol} = -1 \text{ mol} \)

Now we can calculate \( w \):

\[
w = -P\Delta V = -P \left( \Delta n \times \frac{RT}{P} \right) = -\Delta nRT
\]

where \( \Delta n = -1 \text{ mol} \)

\[
R = 8.3145 \text{ J K}^{-1} \text{ mol}^{-1}
\]

\[
T = 25^\circ C + 273 = 298 \text{ K}
\]
Thus \[ w = -(-1 \text{ mol}) \left( 8.3145 \frac{J}{K \text{ mol}} \right) (298 \text{ K}) = 2.48 \text{ kJ} \]

\[ \Delta H = q_P = -198 \text{ kJ} \]

Using the values of \( q \) and \( w \), we can calculate \( \Delta E \):

\[ \Delta E = q + w = \Delta H + w = -198 \text{ kJ} + 2.48 \text{ kJ} = -196 \text{ kJ} \]

Note that \( \Delta E \) and \( \Delta H \) are different for this case because the volume changes (and therefore work occurs).
Calorimetry experiments can also be performed at constant volume

$$\Delta E = q_V + W (=0) = q_V \text{ (constant volume)}$$

To measure the energy of combustion of octane ($C_8H_{18}$). A 0.5269 g of octane is placed in a bomb calorimeter (heat capacity = 11.3 kJ/°C)
Energy released = temperature increase \times \text{energy required to change by the reaction} \times \text{the temperature by 1°C} \\
= \Delta T \times \text{heat capacity of calorimeter} \\
= 2.25°C \times 11.3 \text{ kJ/°C} = 25.4 \text{ kJ}

This means that 25.4 \text{ kJ} of energy was released by the combustion of 0.5269 \text{ g} of octane. The number of moles of octane is

\[0.5269 \text{ g octane} \times \frac{1 \text{ mol octane}}{114.2 \text{ g octane}} = 4.614 \times 10^{-3} \text{ mol octane}\]
Since 25.4 kJ of energy was released for $4.614 \times 10^{-3}$ mol of octane, the energy released per mole is

$$\frac{25.4 \text{ kJ}}{4.614 \times 10^{-3} \text{ mol}} = 5.50 \times 10^3 \text{ kJ/mol}$$

Since the reaction is exothermic, $\Delta E$ is negative:

$$\Delta E_{\text{combustion}} = -5.50 \times 10^3 \text{ kJ/mol}$$

Note that since no work is done in this case, $\Delta E$ is equal to the heat:

$$\Delta E = q + w = q$$

$$= -5.50 \times 10^3 \text{ kJ/mol}$$
Figure 9.9: Schematic of a bomb calorimeter
Example 9.5

It has been suggested that hydrogen gas obtained from the decomposition of water might be a substitute for natural gas (principally methane). To compare the energies of combustion of these fuels, the following experiment was carried out, using a bomb calorimeter with a heat capacity of 11.3 kJ/°C. When a 1.50-g sample of methane gas was burned with excess oxygen in the calorimeter, the temperature increased by 7.3°C. When a 1.15-g sample of hydrogen gas was burned with excess oxygen, the temperature increase was 14.3°C. Calculate the energy of combustion (per gram) for hydrogen and methane.
**Solution**

We calculate the energy of combustion for methane, using the heat capacity of the calorimeter (11.3 kJ/°C) and the observed temperature increase of 7.3°C.

\[
\text{Energy released in the combustion of } 1.50 \text{ g of CH}_4 = (11.3 \text{ kJ/°C})(7.3°\text{C}) = 83 \text{ kJ}
\]

\[
\text{Energy released in the combustion of } 1 \text{ g of CH}_4 = \frac{83 \text{ kJ}}{1.50 \text{ g}} = 55 \text{ kJ/g}
\]
Similarly, for hydrogen,

Energy released in the combustion of 1.15 g of H\(_2\) = (11.3 kJ/°C)(14.3°C)

= 162 kJ

Energy released in the combustion of 1 g of H\(_2\) = \(\frac{162 \text{ kJ}}{1.15 \text{ g}}\) = 141 kJ/g

The energy released by the combustion of 1 g of hydrogen is approximately 2.5 times that for 1 g of methane, indicating that hydrogen gas is a potentially useful fuel.
9.5 Hess’s law

In going from a particular set of reactants to products, the change in enthalpy is the same whether the reaction takes place in one step or in a series of steps (Hess’s law).
\[ \text{N}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{NO}_2(g) \quad \Delta H_1 = 68 \text{ kJ} \]

This reaction can also be carried out in two distinct steps, with enthalpy changes designated by \( \Delta H_2 \) and \( \Delta H_3 \):

\[
\begin{align*}
\text{N}_2(g) + \text{O}_2(g) & \rightarrow 2\text{NO}(g) \quad \Delta H_2 = 180 \text{ kJ} \\
2\text{NO}(g) + \text{O}_2(g) & \rightarrow 2\text{NO}_2(g) \quad \Delta H_3 = -112 \text{ kJ}
\end{align*}
\]

Net reaction: \[ \text{N}_2(g) + 2\text{O}_2(g) \rightarrow 2\text{NO}_2(g) \quad \text{H}_2 + \Delta H_3 = 68 \text{ kJ} \]

Note that the sum of these two steps gives the net, or overall, reaction and that

\[ \Delta H_1 = \Delta H_2 + \Delta H_3 = 68 \text{ kJ} \]
Figure 9.10: Principle of Hess's law

Two-step reaction

\[ \begin{align*}
\text{O}_2(g), 2\text{NO}(g) & \quad \Delta H_2 = 180 \text{ kJ} \\
\text{N}_2(g), 2\text{O}_2(g) & \quad \Delta H_1 = 68 \text{ kJ} = \Delta H_2 + \Delta H_3 = 180 \text{ kJ} - 112 \text{ kJ}
\end{align*} \]

\[ \begin{align*}
2\text{NO}_2(g) & \quad \Delta H_3 = -112 \text{ kJ} \\
\text{N}_2(g), 2\text{O}_2(g) & \quad \text{One-step reaction}
\end{align*} \]
Characteristics of enthalpy changes

Two characteristics of $\Delta H$ for a reaction:

1. If a reaction is reversed, the sign of $\Delta H$ is also reversed.

2. $\Delta H$ is directly proportional to the quantities (coefficients) of reactants & products in a reaction.
Example 9.6

Diborane ($\text{B}_2\text{H}_6$) is a highly reactive boron hydride, which was once considered as a possible rocket fuel for the U.S. space program. Calculate $\Delta H$ for the synthesis of diborane from its elements, according to the equation

$$2\text{B}(s) + 3\text{H}_2(g) \rightarrow \text{B}_2\text{H}_6(g)$$

using the following data:

<table>
<thead>
<tr>
<th>Reaction</th>
<th>$\Delta H$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) $2\text{B}(s) + \frac{3}{2}\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s)$</td>
<td>$-1273$ kJ</td>
</tr>
<tr>
<td>(b) $\text{B}_2\text{H}_6(g) + 3\text{O}_2(g) \rightarrow \text{B}_2\text{O}_3(s) + 3\text{H}_2\text{O}(g)$</td>
<td>$-2035$ kJ</td>
</tr>
<tr>
<td>(c) $\text{H}_2(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{H}_2\text{O}(l)$</td>
<td>$-286$ kJ</td>
</tr>
<tr>
<td>(d) $\text{H}_2\text{O}(l) \rightarrow \text{H}_2\text{O}(g)$</td>
<td>$44$ kJ</td>
</tr>
</tbody>
</table>
(a) \[ 2B(s) + \frac{3}{2}O_2(g) \rightarrow B_2O_3(s) \] \[ \Delta H = -1273 \text{ kJ} \]

-(b) \[ B_2O_3(s) + 3H_2O(g) \rightarrow B_2H_6(g) + 3O_2(g) \] \[ \Delta H = -( -2035 \text{ kJ}) \]

Sum: \[ B_2O_3(s) + 2B(s) + \frac{3}{2}O_2(g) + 3H_2O(g) \rightarrow B_2O_3(s) + B_2H_6(g) + 3O_2(g) \] \[ \Delta H = 762 \text{ kJ} \]

Deleting the species that occur on both sides gives

\[ 2B(s) + 3H_2O(g) \rightarrow B_2H_6(g) + \frac{3}{2}O_2(g) \] \[ \Delta H = 762 \text{ kJ} \]

\[ 2B(s) + 3H_2O(g) \rightarrow B_2H_6(g) + \frac{3}{2}O_2(g) \] \[ \Delta H = 762 \text{ kJ} \]

\[ 3 \times (c) \quad 3[H_2(g) + \frac{1}{2}O_2(g) \rightarrow H_2O(l)] \] \[ \Delta H = 3(-286 \text{ kJ}) \]

Sum: \[ 2B(s) + 3H_2(g) + \frac{3}{2}O_2(g) + 3H_2O(g) \rightarrow B_2H_6(g) + \frac{3}{2}O_2(g) + 3H_2O(l) \] \[ \Delta H = -96 \text{ kJ} \]
2B(s) + 3H₂(g) + 3H₂O(g) → B₂H₆(g) + 3H₂O(l)  \[ \Delta H = -96 \text{ kJ} \]

\[
3 \times (d) \\
3[H_2O(l) \rightarrow H_2O(g)] \\
\Delta H = 3(44 \text{ kJ})
\]

\[
2B(s) + 3H₂(g) + 3H₂O(g) + 3H₂O(l) \rightarrow B₂H₆(g) + 3H₂O(l) + 3H₂O(g) \\
\Delta H = +36 \text{ kJ}
\]

This step gives the reaction required by the problem:

\[
2B(s) + 3H₂(g) \rightarrow B₂H₆(g) \quad \boxed{\Delta H = +36 \text{ kJ}}
\]

Thus \( \Delta H \) for the synthesis of 1 mol of diborane is +36 kJ.

(a) - (b) + 3(c) + 3(d)
Firewalking: Magic or Science?

For millennia people have been amazed at the ability of Eastern mystics to walk across beds of glowing coals without any apparent discomfort. Even in the United States thousands of people have performed feats of firewalking as part of motivational seminars. How is this feat possible? Do firewalkers have supernatural powers?

Actually, there are sound scientific explanations of why firewalking is possible. The first important factor concerns the heat capacity of feet. Because human tissue is mainly composed of water, it has a relatively large specific heat capacity. This means that a large amount of energy must be transferred from the coals to significantly change the temperature of the feet. During the brief contact between feet and coals, there is relatively little time for energy flow, so the feet do not reach a high enough temperature to cause damage.

Second, although the surface of the coals has a very high temperature, the red-hot layer is very thin. Therefore, the quantity of energy available to heat the feet is smaller than might be expected. This factor points out the difference between temperature and heat. Temperature reflects the intensity of the random kinetic energy in a given sample of matter. The amount of energy available for heat flow, on the other hand, depends on the quantity of matter at a given temperature—10 g of matter at a given temperature contains ten times as much thermal energy as 1 g of the same matter. For example, the tiny spark from a sparkler does not hurt when it hits your hand. The spark has a very high temperature but has so little mass that no significant energy transfer occurs to your hand. This same argument applies to the very thin hot layer on the coals.

A third factor that aids firewalkers is the presence of moisture from the perspiration on the feet of the presumably tense firewalker. In addition, because firewalking is often done at night, with moist grass surrounding the bed of coals, the firewalker's feet are probably damp before the walk. Vaporization of this moisture consumes some of the energy from the hot coals.

Thus, although firewalking is an impressive feat, there are several sound scientific reasons why anyone should be able to do it with the proper training and a properly prepared bed of coals.
Explanations:

1. Large heat capacity of feet because of water.
2. Although the surface of the coals has a very high temp, the red-hot layer is very thin. *Temp reflects the intensity of the random kinetic energy in a given sample of matter. The amount of energy available for heat flow, depends on the quantity of matter at a given temp.*
3. Vaporization of the moisture consumes some of the energy from the hot coals.
9.6 Standard enthalpies of formation

*Summary: definitions of standard states*

- For a gas the standard state is a pressure of exactly 1 \text{ atm}.

- For a solution the standard state is a conc of exactly 1 \text{ M (1 atm)}. 
• For a liquid & solid (*condensed state*), the standard state is the *pure liquid or solid*.

• For an element the standard state is the form in which the *element exists (is more stable)* under conditions of 1 atm & 25°C.
The importance of tabulated $\Delta H_f^\circ$ values is that enthalpies for many reactions can be calculated.
Fig. 9.11: Schematic diagram of the energy changes

\[ \text{CH}_4(g) + 2\text{O}_2(g) \rightarrow \text{CO}_2(g) + 2\text{H}_2\text{O}(l) \]

\[ \Delta H^\circ_{(a)} = 75 \text{ kJ} \]
\[ \Delta H^\circ_{(b)} = 0 \text{ kJ} \]
\[ \Delta H^\circ_{(c)} = -394 \text{ kJ} \]
\[ \Delta H^\circ_{(d)} = -572 \text{ kJ} \]
$$\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}$$

$$= -\Delta H_f^\circ \ [\text{for CH}_4(g)] + 0 + \Delta H_f^\circ \ [\text{for CO}_2(g)]$$

$$+ 2 \times \Delta H_f^\circ \ [\text{for H}_2\text{O}(l)]$$

$$= -(-75 \ \text{kJ}) + 0 + (-394 \ \text{kJ}) + (-572 \ \text{kJ})$$

$$= -891 \ \text{kJ}$$
Summary:
key concepts for doing enthalpy calculations

• When a reaction is reversed, the magnitude of $\Delta H$ remains the same, but the sign changes.

• When the balanced eq for a reaction is multiplied by an integer, the value of $\Delta H$ must be multiplied by the same integer.
• The change in enthalpy for a given reaction can be calculated from the enthalpies of formation of the reactants & products:

\[ \Delta H^\circ_{\text{reaction}} = \Sigma \Delta H^\circ_f \text{ (products)} - \Sigma \Delta H^\circ_f \text{ (reactants)} \]

• Elements in their standard states are not included in the \( \Delta H_{\text{reaction}} \) calculation. That is, \( \Delta H^\circ_f \) for an element in its standard state is zero.
Using the standard enthalpies of formation listed in Table 9.4, calculate the standard enthalpy change for the overall reaction that occurs when ammonia is burned in air to form nitrogen dioxide and water. This is the first step in the manufacture of nitric acid.

\[ 4\text{NH}_3(g) + 7\text{O}_2(g) \rightarrow 4\text{NO}_2(g) + 6\text{H}_2\text{O}(l) \]
Figure 9.12: Pathway for the combustion of ammonia
We now add the $\Delta H^\circ$ values for the steps to obtain $\Delta H^\circ$ for the overall reaction:

$$
\Delta H^\circ_{\text{reaction}} = \Delta H^\circ_{(a)} + \Delta H^\circ_{(b)} + \Delta H^\circ_{(c)} + \Delta H^\circ_{(d)}
$$

$$
= 4 \times -\Delta H^\circ_f [\text{for NH}_3(g)] + 0 + 4 \times \Delta H^\circ_f [\text{for NO}_2(g)] \\
+ 6 \times \Delta H^\circ_f [\text{for H}_2\text{O}(l)]
$$

$$
= 4 \times \Delta H^\circ_f [\text{for NO}_2(g)] + 6 \times \Delta H^\circ_f [\text{for H}_2\text{O}(l)] \\
- 4 \times \Delta H^\circ_f [\text{for NH}_3(g)]
$$

$$
= \Delta H^\circ_f (\text{products}) - \Delta H^\circ_f (\text{reactants})
$$

Remember that elemental reactants and products do not need to be included, since $\Delta H^\circ_f$ for an element in its standard state is zero. Note that we have again obtained Equation (9.1). The final solution is

$$
\Delta H^\circ_{\text{reaction}} = 6 \times (-286 \text{ kJ}) + 4 \times (34 \text{ kJ}) - 4 \times (-46 \text{ kJ})
$$

$$
= -1396 \text{ kJ}
$$
Example 9.8

Methanol (CH₃OH) is sometimes used as a fuel in high-performance engines. Using the data in Table 9.4, compare the standard enthalpy of combustion per gram of methanol with that of gasoline. Gasoline is actually a mixture of compounds, but assume for this problem that gasoline is pure liquid octane (C₈H₁₈).

Solution

The combustion reaction for methanol is

$$2\text{CH}_3\text{OH}(l) + 3\text{O}_2(g) \rightarrow 2\text{CO}_2(g) + 4\text{H}_2\text{O}(l)$$

Using the standard enthalpies of formation from Table 9.4 and Equation (9.1), we have

$$\Delta H^o_{\text{reaction}} = 2 \times \Delta H^o_f [\text{for CO}_2(g)] + 4 \times \Delta H^o_f [\text{for H}_2\text{O}(l)]$$

$$- 2 \times \Delta H^o_f [\text{for CH}_3\text{OH}(l)]$$

$$= 2 \times (-394 \text{ kJ}) + 4 \times (-286 \text{ kJ}) - 2 \times (-239 \text{ kJ})$$

$$= -1454 \text{ kJ}$$
\[
\frac{-1454 \text{ kJ}}{64.0 \text{ g}} = -22.7 \text{ kJ/g}
\]

The combustion reaction for octane is

\[
2C_8H_{18}(l) + 25O_2(g) \rightarrow 16CO_2(g) + 18H_2O(l)
\]

Using the standard enthalpies of formation from Table 9.4 and Equation (9.1) we have

\[
\Delta H^o_{\text{reaction}} = 16 \times \Delta H^o_f \text{ [for CO}_2(g)\text{]} + 18 \times \Delta H^o_f \text{ [for H}_2O(l)\text{]} - 2 \times \Delta H^o_f \text{ [for C}_8\text{H}_{18}(l)\text{]}
\]

\[
= 16 \times (-394 \text{ kJ}) + 18 \times (-286 \text{ kJ}) - 2 \times (-269 \text{ kJ})
\]

\[
= -1.09 \times 10^4 \text{ kJ}
\]

This value is the amount of heat evolved when 2 mol of octane burns. Since the molar mass of octane is 114.2 g/mol, the enthalpy of combustion per gram of octane is

\[
\frac{-1.09 \times 10^4 \text{ kJ}}{2(114.2 \text{ g})} = -47.7 \text{ kJ/g}
\]
The enthalpy of combustion per gram of octane is about twice that per gram of methanol. On this basis, gasoline appears to be superior to methanol for use in a racing car, where weight considerations are usually very important. *Why, then, is methanol used in racing cars?* The answer is that methanol burns much more smoothly than gasoline in high-performance engines, and this advantage more than compensates for its weight disadvantage.
### TABLE 9.5  Formulas and Names for Some Common Hydrocarbons

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH₄</td>
<td>Methane</td>
</tr>
<tr>
<td>C₂H₆</td>
<td>Ethane</td>
</tr>
<tr>
<td>C₃H₈</td>
<td>Propane</td>
</tr>
<tr>
<td>C₄H₁₀</td>
<td>Butane</td>
</tr>
<tr>
<td>C₅H₁₂</td>
<td>Pentane</td>
</tr>
<tr>
<td>C₆H₁₄</td>
<td>Hexane</td>
</tr>
<tr>
<td>C₇H₁₆</td>
<td>Heptane</td>
</tr>
<tr>
<td>C₈H₁₈</td>
<td>Octane</td>
</tr>
</tbody>
</table>
### TABLE 9.6 Uses of the Various Petroleum Fractions

<table>
<thead>
<tr>
<th>Petroleum Fraction in Terms of Numbers of Carbon Atoms</th>
<th>Major Uses</th>
</tr>
</thead>
<tbody>
<tr>
<td>C&lt;sub&gt;5&lt;/sub&gt;–C&lt;sub&gt;10&lt;/sub&gt;</td>
<td>Gasoline</td>
</tr>
<tr>
<td>C&lt;sub&gt;10&lt;/sub&gt;–C&lt;sub&gt;18&lt;/sub&gt;</td>
<td>Kerosene</td>
</tr>
<tr>
<td></td>
<td>Jet fuel</td>
</tr>
<tr>
<td>C&lt;sub&gt;15&lt;/sub&gt;–C&lt;sub&gt;25&lt;/sub&gt;</td>
<td>Diesel fuel</td>
</tr>
<tr>
<td></td>
<td>Heating oil</td>
</tr>
<tr>
<td></td>
<td>Lubricating oil</td>
</tr>
<tr>
<td>&gt; C&lt;sub&gt;25&lt;/sub&gt;</td>
<td>Asphalt</td>
</tr>
</tbody>
</table>
9.8 New energy resources

• Coal conversion
• Hydrogen as a fuel
• Other energy alternatives - ethanol & methanol
Figure 9.15: Coal gasification

Coal (C) + steam [H₂O(g)] + air [O₂(g)]

Heat

CH₄(g), CO(g), CO₂(g), H₂(g), H₂O(g) + sulfur-containing impurities (sulfur compounds)

Separate

CO(g) + H₂O(g) → CO₂(g) + H₂(g)

CO(g) + 3H₂(g) → CH₄(g) + H₂O(g)

Remove CO₂, H₂O, impurities

CH₄(g)

CH₄(g) Syngas [CO(g), H₂(g)]
Example 9.9

Assuming that the combustion of hydrogen gas provides three times as much energy per gram as gasoline, calculate the volume of liquid H₂ (density = 0.0710 g/mL) required to furnish the energy contained in 80.0 L (about 20 gal) of gasoline (density = 0.740 g/mL). Calculate also the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C.

Solution
The mass of 80.0 L of gasoline is

\[
80.0 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{0.740 \text{ g}}{\text{mL}} = 59,200 \text{ g}
\]

Since H₂ furnishes three times as much energy per gram as gasoline, only one-third as much liquid hydrogen is needed to furnish the same energy:

\[
\text{Mass of H}_2(l) \text{ needed} = \frac{59,200 \text{ g}}{3} = 19,700 \text{ g}
\]
Since density = mass/volume, volume = mass/density, and the volume of H₂ needed is

\[ V = \frac{19,700 \text{ g}}{0.0710 \text{ g/mL}} = 2.77 \times 10^5 \text{ mL} = 277 \text{ L} \]

Thus 277 L of liquid H₂ is needed to furnish the same energy of combustion as 80.0 L of gasoline.

To calculate the volume that this hydrogen would occupy as a gas at 1.00 atm and 25°C, we use the ideal gas law:

\[ PV = nRT \]

In this case \( P = 1.00 \text{ atm}, \) \( T = 273 + 25°C = 298 \text{ K}, \) and \( R = 0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1}. \) Also,

\[ n = 19,700 \text{ g H}_2 \times \frac{1 \text{ mol H}_2}{2.02 \text{ g H}_2} = 9.75 \times 10^3 \text{ mol H}_2 \]
Thus \[ V = \frac{nRT}{P} = \frac{(9.75 \times 10^3 \text{ mol})(0.08206 \text{ L atm K}^{-1} \text{ mol}^{-1})(298 \text{ K})}{1.00 \text{ atm}} \]

\[ = 2.38 \times 10^5 \text{ L} = \boxed{238,000 \text{ L}} \]

At 1 atm and 25°C, the hydrogen gas needed to replace 20 gal of gasoline occupies a volume of 238,000 L.
Possible solution:

\[ \text{H}_2(g) + \text{M}(s) \rightarrow \text{MH}_2(s) \]

\[ \text{MH}_2(s) \rightarrow \text{M}(s) + \text{H}_2(g) \]