Skills to develop

• Change the enthalpy of reaction when the equation changes
• Interpret Hess’s law
• Apply the principle of conservation of energy, Hess’s law, to solve problems.
• Sketch an energy diagram for related reactions
• Use a diagram to explain Hess’s law

Hess’s Law

Germain Henri Hess (1802 - 1850) is important primarily for his thermochemical studies. Hess’ Law states that the heat evolved or absorbed in a chemical process is the same whether the process takes place in one or in several steps. This is also known as the law of constant heat summation. To illustrate Hess’s law, the thermal equations and the energy level diagrams are shown below.

<table>
<thead>
<tr>
<th>Thermal equations</th>
<th>Hess’s law energy level diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{A + B = AB}, \Delta H_1 )</td>
<td>( \text{A + 2 B} )</td>
</tr>
<tr>
<td>( \text{AB + B = AB}_2, \Delta H_2 )</td>
<td>( \Delta H_1 )</td>
</tr>
<tr>
<td>( \text{A + 2 B = AB}_2 )</td>
<td>( \Delta H_2 )</td>
</tr>
<tr>
<td>( \Delta H_{1.2} = \Delta H_1 + \Delta H_2 )</td>
<td>( \text{AB} )</td>
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</tbody>
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Chemical energy and Hess’s law

The standard enthalpy of reaction and standard enthalpy of formation introduced in Chemical Energy are very useful chemical properties. We have already mentioned some basic rules regarding the quantities \( \Delta H \), \( \Delta H^\circ \), and \( \Delta H_f \) and their preceding equations.

If both sides of the equations are multiplied by a factor to alter the number of moles, \( \Delta H \), \( \Delta H^\circ \), or \( \Delta H_f \) for the equation should be multiplied by the same factor, since they are quantities per equation as written. Thus, for the equation

\( \text{C_{(graphite)}) + 0.5, O_2 rightarrow CO, \ hspace{20px} \mathit{\Delta H}^\circ = -110\ kJ/mol} \).

We can write it in any of the following forms:

\( \text{C_{(graphite)}) + 0.5, O_2 rightarrow CO, \ hspace{20px} \mathit{\Delta H}^\circ = -110\ kJ/mol} \).
2 C_{(graphite)} + O_2 \rightarrow 2 CO, \mathit{\Delta H}^\circ = -220 \text{ kJ/mol} (multiplied by 2) \\
6 C_{(graphite)} + 3 O_2 \rightarrow 6 CO, \mathit{\Delta H}^\circ = -660 \text{ kJ/mol} (multiplied by 6)\)

For the reverse reaction, the signs of these quantities are changed (multiply by -1). The equation implies the following:

\[
\text{CO} \rightarrow C_{(graphite)} + 0.5 O_2, \mathit{\Delta H}^\circ = 110 \text{ kJ/mol}
\]
\[
2 \text{CO} \rightarrow 2 C_{(graphite)} + O_2, \mathit{\Delta H}^\circ = 220 \text{ kJ/mol}
\]

Hess's law states that energy changes are state functions. The amount of energy depends only on the states of the reactants and the state of the products, not on the intermediate steps. Energy (enthalpy) changes in chemical reactions are the same, regardless of whether the reactions occur in one or several steps. The total energy change in a chemical reaction is the sum of the energy changes in its many steps leading to the overall reaction.

For example, in the diagram below, we look at the oxidation of carbon into \(\text{CO}\) and \(\text{CO}_2\). The direct oxidation of carbon (graphite) into \(\text{CO}_2\) yields an enthalpy of -393 kJ/mol. When carbon is oxidized into \(\text{CO}\) and then \(\text{CO}\) is oxidized to \(\text{CO}_2\), the enthalpies are -110 and -283 kJ/mol respectively. The sum of enthalpy in the two steps is exactly -393 kJ/mol, same as the one-step reaction.

The two-step reactions are:

\[
\text{C + } \dfrac{1}{2} \text{O}_2 \rightarrow \text{CO}, \mathit{\Delta H}^\circ = -110 \text{ kJ/mol} \]
\[
\text{CO} + \dfrac{1}{2} \text{O}_2 \rightarrow \text{CO}_2, \mathit{\Delta H}^\circ = -283 \text{ kJ/mol} \]

Adding the two equations together and canceling out the intermediate, \(\text{CO}\), on both sides leads to

\[
\mathit{\Delta H}^\circ = (-110)+(-283) = -393 \text{ kJ/mol} \]

The real merit is actually to evaluate the enthalpy of formation of \(\text{CO}\) as we shall see soon.

**Application of Hess's Law**

Hess's law can be applied to calculate enthalpies of reactions that are difficult to measure. In the above example, it is
very difficult to control the oxidation of graphite to give pure \(\ce{CO}\). However, enthalpy for the oxidation of graphite to \(\ce{CO2}\) can easily be measured. So can the enthalpy of oxidation of \(\ce{CO}\) to \(\ce{CO2}\). The application of Hess's law enables us to estimate the enthalpy of formation of \(\ce{CO}\). Since,

\[
\begin{align*}
C + O_2 \rightarrow CO_2, & \quad \Delta H^\circ = -393 \text{ kJ/mol} \\
CO + \dfrac{1}{2} O_2 \rightarrow CO_2, & \quad \Delta H^\circ = -283 \text{ kJ/mol}
\end{align*}
\]

Subtracting the second equation from the first gives

\[
C + \dfrac{1}{2} O_2 \rightarrow CO, \quad \Delta H^\circ = -393 - (-283) = -110 \text{ kJ/mol}
\]

The equation shows the standard enthalpy of formation of \(\ce{CO}\) to be -110 kJ/mol.

Application of Hess's law enables us to calculate \(\Delta H^\circ\), \(\Delta H_f^\circ\), and \(\Delta H_f\) for chemical reactions that impossible to measure, providing that we have all the data of related reactions.

Some more examples are given below to illustrate the applications of Hess Law.

Example 1

The enthalpy of combustion for \(\ce{H_2}\), \(\ce{C_{\text{(graphite)}}}\) and \(\ce{CH_4}\) are -285.8, -393.5, and -890.4 kJ/mol respectively. Calculate the standard enthalpy of formation \(\Delta H_f\) for \(\ce{CH_4}\).

**Solution:**

Lets interpret the information about enthalpy of formation by writing out the equations:

\[
\begin{align*}
(1) \quad & \mathrm{H_{\text{(g)}} + 0.5\ O_{\text{(g)}} \rightarrow H_2O_{\text{(l)}}}, \quad \Delta H = -285.8 \text{ kJ/mol} \\
(2) \quad & \mathrm{C_{\text{(graphite)}} + O_{\text{(g)}} \rightarrow CO_{\text{(g)}}}, \quad \Delta H = -293.5 \text{ kJ/mol} \\
(3) \quad & \mathrm{CH_{4\text{(g)}} + 2O_{\text{(g)}} \rightarrow CO_{\text{(g)}} + 2H_2O_{\text{(l)}}}, \quad \Delta H = -890.4 \text{ kJ/mol}
\end{align*}
\]

From the above equations, derive

\[
\mathrm{C + 2H_2 \rightarrow CH_4}\]

Answer: \(\Delta H_f = -74.7 \text{ kJ/mol}\)

Hint: \(\Delta H_f = 2 \times \Delta H_1 - \Delta H_2 - \Delta H_3\)

**Discussion:**

Three enthalpies of reactions involved in this Example are standard enthalpies of formation, and one is the enthalpy of combustion. The formation of methane from graphite and hydrogen cannot be achieved easily, and its enthalpy of formation is not directly measurable, but the calculations like this provide the data to be included in thermodynamic data.
The value of -74.4 kJ/mol has been listed in several data sources.

From these data, we can construct an energy level diagram for these chemical combinations as follows:

Example 2

From the following data,

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O} & \hspace{20px} \Delta H = -890\text{ kJ/mol} \\
\text{H}_2\text{O}_{(l)} \rightarrow \text{H}_2\text{O}_{(g)} & \hspace{20px} \Delta H = 44\text{ kJ/mol at 298 K}
\end{align*}
\]

Calculate the enthalpy of the reaction

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

Solution:
Add the two equations to give the third one:

\[
\begin{align*}
\text{CH}_4 + 2\text{O}_2 & \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}_{(l)} \\
\text{add: the equations} & \hspace{20px} \Delta H = -890\text{ kJ/mol} \\
\text{underline}{2\text{H}_2\text{O}_{(l)} \rightarrow 2\text{H}_2\text{O}_{(g)}} & \hspace{20px} \Delta H = 88\text{ kJ/mol} \\
\text{add: the enthalpies}
\end{align*}
\]
\[ CH_4 + 2 O_{\text{(g)}} \rightarrow CO_{\text{(g)}} + 2 H_2O_{\text{(g)}} \]
\[ \Delta H^\circ = -802 \text{ kJ/mol} \]

**Discussion:**
A higher amount of energy (890 vs 802 kJ/mol) is extracted if the exhaust is condensed to liquid water. The exhaust from high efficiency furnace is at lower temperature, and the water vapour is condensed to liquid. However, there is always some lost in a furnace operation.

Example 3

The standard enthalpies of formation of \( \ce{SO2} \) and \( \ce{SO3} \) are -297 and -396 kJ/mol respectively. Calculate the standard enthalpy of reaction for the reaction:

\[ \ce{SO_2 + \frac{1}{2} O_2 \rightarrow SO_3} \]

**Solution:**
In order to show how the chemical reactions take place, and for a better appreciation of the technique of problem solving, we write the equations according to the data given:

\[ \ce{SO_{(g)} \rightarrow S_{(s)} + O_{2(g)} \hspace{20px} \Delta H = 297 \text{ kJ}} \]
\[ S_{(s)} + \frac{3}{2} O_2 \rightarrow SO_3 \hspace{20px} \Delta H = -396 \text{ kJ}} \]

Add the two equations to give

\[ \ce{SO_{2(g)} + \frac{1}{2} O_2 \rightarrow SO_3 \hspace{20px} \Delta H = -99 \text{ kJ}} \]

**Your turn to work:**
Sketch an energy level diagram for the combinations of substances.

Example 4

From the following enthalpies of reactions:

1. \( \ce{2 O_{(g)} \rightarrow O_{2(g)} \hspace{20px} \Delta H^\circ = -249 \text{ kJ/mol}} \)
2. \( \ce{H_2O_{(g)} \rightarrow H_2O_{(g)} \hspace{20px} \Delta H^\circ = 44 \text{ kJ/mol}\text{ at: 298 K}} \)
3. \( \ce{2 H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)} \hspace{20px} \Delta H^\circ = -803 \text{ kJ/mol}} \)
4. \( \ce{C_{(graphite)} + 2 O_{(g)} \rightarrow CO_{2(g)} \hspace{20px} \Delta H^\circ = -643 \text{ kJ/mol}} \)
5. \( \ce{C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)} \hspace{20px} \Delta H^\circ = -394 \text{ kJ/mol}} \)
6. \( \ce{C_{(graphite)} + 2 H_{2(g)} \rightarrow CH_{4(g)} \hspace{20px} \Delta H^\circ = -75 \text{ kJ/mol}} \)
7. \[2 \text{H} \rightarrow \text{H}_2 \hspace{20px} \Delta H^\circ = -436 \text{kJ/mol}\]

8. \[\text{H}_2\text{O} \rightarrow \text{H}_2\text{O} \hspace{20px} \Delta H = 41 \text{kJ/mol at 373 K, non-standard condition}\]

**Calculate the heat of combustion of methane into gaseous \(\text{H}_2\text{O}\).**

**Solution:**

-2(1) + 2(3) + (4) - (6) - 2(7) gives

\[\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O}\]

and therefore,

\[
\Delta H = -2 \times (-249) + 2 \times (-803) + (-643) - (-75) - 2(-436) = -804 \text{kJ/mol}
\]

**Discussion:**

Work out the details yourself and check the result. The calculation is rather complicated. Reading it will not be able to master the technique. Data from equations 2, 5 and 8 are not required. Often, you have to select suitable data from a Table of Standard Enthalpy of Formation in problem solving.

Compare to result of Example 2, this result differ slightly, due to a different set of data being used. The difference is 0.2%.

One method is to re-write the key equations as follows and then add them to cancel out undesirable compound on both sides. Practice the cancellation of the formula yourself.

\[
\begin{align}
\text{CH}_4 &\rightarrow \text{C}_{\text{graphite}} + 2 \text{H}_2 \\
\text{C}_{\text{graphite}} &+ 2 \text{O}_2 \rightarrow \text{CO}_2 \\
2 \text{O}_2 &\rightarrow 4 \text{O} \\
4 \text{H} &+ 2 \text{O}_2 \rightarrow 2 \text{H}_2\text{O}
\end{align}
\]

\[\text{add all equations} \hspace{10px} \Delta H^\circ = 872 \text{kJ/mol}\]

\[\text{add all } \Delta H\text{s} \hspace{30px} \text{KJ/mol}\]

\[\Delta H\text{s} \hspace{10px} \text{KJ/mol}\]

\[\text{add all } \Delta H\text{s} \hspace{30px} \text{KJ/mol}\]
\[
\text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O} \quad \Delta H^\circ = -804 \text{ kJ/mol}
\]

## Confidence Building Questions

1. **The enthalpy of the reaction**

   \[
   \text{CH}_4 + 2 \text{O}_2 \rightarrow \text{CO}_2 + 2 \text{H}_2\text{O}
   \]

   is -890.4 kJ/mol. What is the enthalpy for the reaction,

   \[
   2 \text{CO}_2 + 4 \text{H}_2\text{O} \rightarrow 2 \text{CH}_4 + 4 \text{O}_2
   \]

   Hint: 1780.8 kJ

   **Skill:**

   Change the enthalpy of reaction when the equation changes. What is the enthalpy for the reaction,

   \[
   \text{CO}_2 + 2 \text{H}_2\text{O} \rightarrow \text{CH}_4 + 2 \text{O}_2
   \]

2. **The standard enthalpies of formation of \(\text{SO}_2\) and \(\text{SO}_3\) are -297 and -396 respectively. What is the standard enthalpy of the reaction**

   \[
   \text{SO}_3 \rightarrow \text{SO}_2 + \frac{1}{2} \text{O}_2
   \]

   Hint: 99

   **Skill:**

   See Example 3. Sketch an energy diagram for related reactions.

3. **The enthalpies of formation of \(\text{H}_2\text{O}\), \(\text{H}_2\text{S}\), and \(\text{SO}_2\) are -285.8, -20.6 and -296.8 kJ/mol respectively. Calculate the standard enthalpy of change for the reaction,**

   \[
   2 \text{H}_2\text{S} + \text{SO}_2 \rightarrow 3 \text{S} + 2 \text{H}_2\text{O}
   \]

   **Skill:**

   Apply Hess's law to calculate standard enthalpy of reaction from standard enthalpies of formation. There are more than one way to solve the problem. One of the way is solve \(\Delta H^\circ\) in the following:

   \[
   \begin{alignat}{2}
   \end{alignat}
   \]

All reactants and products are at their standard states.

Hint: -233.6 kJ
Thus, $\Delta H^\circ = ?$ Use your algebra skill.

4. The enthalpies of formation of $\ce{H2O}$, $\ce{H2S}$, and $\ce{SO2}$ are -285.8, -20.6 and -296.8 kJ/mol respectively. Calculate the enthalpy of reaction for

$$\ce{SO2 \rightarrow S + O2}$$

All reactants and products are at their standard states.

Hint: 296.8 kJ

Skill:
Apply Hess's law to calculate standard enthalpy of reaction from standard enthalpies of formation. There are more than one way to solve the problem.

5. From the following enthalpies of reactions:

1. $\ce{2 O_{(g)} \rightarrow O_{2(g)}} \Delta H^\circ = \mathrm{-249\: kJ/mol}$
2. $\ce{2 H_{(g)} \rightarrow H_{2(g)}} \Delta H^\circ = \mathrm{-436\: kJ/mol}$
3. $\ce{H_2O_{(l)} \rightarrow H_2O_{(g)}} \Delta H = \mathrm{41 kJ/mol at 373 K, non-standard condition}$
4. $\ce{H2O_{(l)} \rightarrow H_2O_{(g)}} \Delta H^\circ = \mathrm{44 kJ/mol at 298 K}$
5. $\ce{2 H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)}} \Delta H^\circ = \mathrm{-803\: kJ/mol}$
6. $\ce{C_{(graphite)} + 2 O_{(g)} \rightarrow CO_{2(g)}} \Delta H^\circ = \mathrm{-643\: kJ/mol}$
7. $\ce{C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}} \Delta H^\circ = \mathrm{-394\: kJ/mol}$
8. $\ce{C_{(graphite)} + 2 H_{2(g)} \rightarrow CH_{4(g)}} \Delta H^\circ = \mathrm{-75\: kJ/mol}$

What is the enthalpy of the reaction,

$$\ce{2 H_{(g)} + O_{(g)} \rightarrow 2 H2O_{(g)}} \Delta H^\circ = \mathrm{?}$$

Hint: -485 kJ

Skill:
Select suitable data from a Table of Standard Enthalpy of reaction to solve a problem.

6. From the following enthalpies of reactions:

1. $\ce{2 O_{(g)} \rightarrow 2 O_{2(g)}} \Delta H^\circ = \mathrm{-249\: kJ/mol}$
2. \( \ce{2 H_{(g)} \rightarrow H_2(g)} \hspace{20px} \Delta H^\circ = \text{-436 kJ/mol} \)

3. \( \ce{H_2O_{(l)} \rightarrow H_2O_{(g)}} \hspace{20px} \Delta H = \text{41 kJ/mol at 373 K, non-standard condition}} \)

4. \( \ce{H_2O_{(l)} \rightarrow H_2O_{(g)}} \hspace{20px} \Delta H^\circ = \text{44 kJ/mol at 298 K}} \)

5. \( \ce{2 H_{(g)} + O_{(g)} \rightarrow H_2O_{(g)}} \hspace{20px} \Delta H^\circ = \text{-803 kJ/mol}} \)

6. \( \ce{C_{(graphite)} + 2 O_{(g)} \rightarrow CO_{2(g)}} \hspace{20px} \Delta H^\circ = \text{-643 kJ/mol}} \)

7. \( \ce{C_{(graphite)} + O_{2(g)} \rightarrow CO_{2(g)}} \hspace{20px} \Delta H^\circ = \text{-394 kJ/mol}} \)

8. \( \ce{C_{(graphite)} + 2 H_{2(g)} \rightarrow CH_{4(g)}} \hspace{20px} \Delta H^\circ = \text{-75 kJ/mol}} \)

What is the enthalpy of the reaction,

\( \ce{2 H_{(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)}} \hspace{20px} \Delta H^\circ = ?} \)

Hint: -573 kJ

Skill:
From the result in the previous problem, only one step is required to solve this problem.

7. Some more problems can be asked from the data given above

Hint: Formulate a problem yourself!

Skill:
Review Skills.

Contributors

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