Skills to Develop

- Calculate the enthalpies of reactions from bond energies.
- Calculate the enthalpies of reactions from enthalpies of formation.
- Draw energy level diagrams and use them to calculate enthalpies of reactions.

Enthalpies of Reactions

**Enthalpy of a reaction** or **energy change of a reaction**, \( \Delta H \), is the amount of energy or heat absorbed in a reaction. If the energy is required, \( \Delta H \) is positive, and if energy is released, the \( \Delta H \), is negative.

\[
\begin{array}{c|c}
\text{Products} & \mathbf{DH, \text{ positive for}} \\
\hline
\text{endothermic reaction} & \\
\hline
\text{Reactants} & \\
\end{array}
\]

The enthalpy can be determined by experiment, but estimates can easily be made if bond energies or standard enthalpies of formation for the reactants and products are available.

Using Formulas to Calculate \( \Delta H \)

Due the the definitions of various types of energy related terms, formulas for evaluating enthalpies can be very confusing. For example, the formulas to calculate the enthalpy of a reaction depends on whether bond energies or enthalpies of formation are available.

When standard **enthalpies of formation**, \( H^\circ \), for all products and reactants are available, we have

\[
\text{\textit{H}}_{\text{reaction}} = \text{SUM} (\text{\textit{H}}_{\text{products}}) - \text{SUM} (\text{\textit{H}}_{\text{reactants}})
\]

or if you prefer using symbols

\[
\text{\textit{H}}_{\text{reaction}} = \sum \text{\textit{H}}_{\text{products}} - \sum \text{\textit{H}}_{\text{reactants}}
\]

For simplicity in formulation we use \( H \) to represent \( H^\circ \) in the above formulas.

Because bond energies are defined as the energies required to break the bonds, positive values are usually listed whereas in reality, they are energies released when chemical bonds are formed from respective atoms. Thus, using the bond energies (\( \text{BE} \)) as they are given or defined, the following formula apply:

\[
\text{\textit{H}}_{\text{reaction}} = \text{SUM} (\text{\textit{BE}}_{\text{reactants}}) - \text{SUM} (\text{\textit{BE}}_{\text{products}})
\]
or if you prefer using symbols

\[
\text{\textit{H}_{\text{reaction}} = \sum \text{\textit{BE}}_{\text{reactants}} - \sum \text{\textit{BE}}_{\text{products}}}
\]

These formulas to calculate the enthalpy (heat) of a reaction can be a very confusing and you may easily get an incorrect sign for the value. Thus, remembering formulas is discouraged!

Well, if you use a diagram to help visualize the calculation or write the chemical reaction equations accompanying the thermodynamic values, you will be able to avoid the confusion. In both cases, you are applying the principle of conservation of energy in solving the problems.

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**Calculate Enthalpy of Reaction from Bond Energies**

Due to the principle of conservation of energy the total energy before and after the reaction must not change. Thus, the energy of a reaction released or absorbed in the reaction must come from the difference in bond energies of the products and the reactants.

**Example 1**

The bond energy (kJ) for \(\text{H}_2\), \(\text{F}_2\), and \(\text{HF}\) are 436, 158 and 568 kJ respectively; calculate the enthalpy (energy) of the reaction,

\[
\text{\textit{H}_\text{2(g)} + \text{F}_\text{2(g)} \rightarrow 2 \text{HF}}
\]

**Solution**

Based on the bond energies given, we have

\[
\begin{align}
\text{&H}_2 &\rightarrow 2\text{H} & D = \text{\textit{H}}\text{\textit{\textsc{m}}\text{\textsc{t}}\text{\textsc{i}}\text{\textsc{h}}\text{\textit{\textsc{e}}} 436\text{\textit{\textsc{k}}\text{\textsc{j}}/\text{\textit{\textsc{m}}\text{\textsc{o}}\text{\textit{l}}}} \\
\text{&F}_2 &\rightarrow 2\text{F} & D = \text{\textit{H}}\text{\textit{\textsc{m}}\text{\textit{t}}\text{\textit{h}}\text{\textit{i}}\text{\textit{t}}} 158\text{\textit{\textsc{k}}\text{\textsc{j}}/\text{\textit{\textsc{m}}\text{\textit{l}}}} \\
\text{&2H + 2F} &\rightarrow 2\text{HF} & D = \text{\textit{H}}\text{\textit{\textsc{m}}\text{\textit{t}}\text{\textit{h}}\text{\textit{i}}\text{\textit{t}}} -568\text{\textit{\times2}}\text{\textit{\textsc{k}}\text{\textsc{j}}/\text{\textit{\textsc{m}}\text{\textit{l}}}}
\end{align}
\]

Adding all three equations and energies leads to the following:

\[
\text{\textit{H}_\text{2(g)} + \text{F}_\text{2(g)} \rightarrow 2 \text{HF}} \ \ \ \text{\textit{H}}\text{\textit{\textsc{m}}\text{\textit{t}}\text{\textit{i}}\text{\textit{h}}\text{\textit{t}}} \ -542\text{\textit{\textsc{k}}\text{\textsc{j}}/\text{\textit{\textsc{e}}\text{\textit{q}}\text{\textit{u}\textit{a}}\text{\textit{t}}}}
\]

Note that \(D\) represent bond dissociation energy, and \(H\) the enthalpy of the reaction as written. We use \(\Delta H\) in the last equation to denote enthalpy of change of the overall reaction.

**Discussion**

Since bond energies are given, we use the monoatomic gases as the reference level in this calculation. The energy level diagram shown below illustrates the principle of conservation of energy, and you are expected to have the skill to draw such a diagram.

\[\text{-----2 H(g) + 2 F(g)-----}\]
Calculate Enthalpy of Reaction from Enthalpy of Formation

A similar cycle can be devised to calculate energy of a reaction when the standard enthalpies of formation are given. We illustrate this cycle by an example.

Example 2

Standard enthalpies of formation are: \( \ce{C2H5OH_{(l)}} \) -228, \( \ce{CO2} \) -394, and \( \ce{H2O_{(l)}} \) -286 kJ/mol. Calculate the enthalpy of the reaction,

\[
\ce{C2H5OH + 3 O2 \rightarrow 2 CO2 + 3 H2O})
\]

Solution

From the definition of the enthalpy of formation, we have the following equations and the energy changes of reactions.

\[
\begin{align}
&\ce{\text{C}_2\text{H}_5\text{OH}_{(l)} \rightarrow 2 \text{C}_{(graphite)} + 3 \text{H}_{2(l)} + 0.5 \text{O}_{2(g)}} \quad \Delta H = -228 \text{ kJ/mol} \\
&\ce{2 \text{C}_{(graphite)} + 2 \text{O}_{2(g)} \rightarrow \text{CO}_2(g)} \quad \Delta H = -394 \times 2 \text{ kJ/mol} \\
&\ce{3 \text{H}_{2(g)} + 1.5 \text{O}_{2(g)} \rightarrow 3 \text{H}_2\text{O}_{(l)}} \quad \Delta H = -286 \times 3 \text{ kJ/mol}
\end{align}
\]

Adding all three equations and energies leads to the following:

\[
\ce{\text{C}_2\text{H}_5\text{OH}_{(l)} + 3 \text{O}_2 \rightarrow 2 \text{CO}_2 + 3 \text{H}_2\text{O}_{(l)}} \quad \Delta \text{H} = -1418 \text{ kJ/mol}
\]

Discussion

Since the standard enthalpy of formation uses the elements as the standard, we put the elements on the top as a common level of 0 energy. The enthalpies of formation are negative, and we have the following diagram.

Thus, the enthalpy of reaction is the difference between the level of

\[
\ce{---C2H5OH +3 O2---}
\]

and

\[
-2 \text{CO}_2 + 3 \text{H}_2\text{O}.\]

---2 C(graphite) + 3 H2 + 3.5 O2(g)---
|                                  |
|                                  | -228 kJ
|                                  |
---C2H5OH + 3 O2---
|\(\Delta H\) = -394*2 - 286*3    |
|\(-228\)                         |
|\(-1418 \text{ kJ}\)            |
------------------2 CO2 + 3 H2O------------------

A Footnote

Due to the definitions, the enthalpies of formation are negative values whereas the bond energies are given as positive values. Thus, calculations using these two types of data have different signs.

You can use the diagramatic method to solve these types of problems as given in the discussions above. Using the diagrams shown indicates clearly what should be the sign of the results. When the reaction is from a higher level to a lower level, the enthalpy of reaction should be negative (downward arrow). If you reverse the direction of the reaction, you also change the sign of the enthalpy of the reaction.

Confidence Building Questions

1. **Calculate the heat of reaction for**
   
   \[\ce{2 H2 + O2 \rightarrow 2 H2O}\]
   
   **Bond energies:** \(\ce{H2}\) 436 kJ/mol, \(\ce{O2}\) 498, \(\ce{HO}\) 463 kJ/mol
   
   Hint: \(\text{4x463 + 498 + 2x436}\)
   
   **Discussion** - Note that in this problem, you are asked to calculate the heat of reaction, but the heat of formation is -241 kJ/mol.

2. **Calculate the heat of reaction for**
   
   \[\ce{H2 + Cl2 \rightarrow 2 HCl}\]
   
   **Bond energies:** \(\ce{H2}\) 436 kJ/mol, \(\ce{O2}\) 498, \(\ce{HO}\) 463, \(\ce{Cl2}\) 243, \(\ce{HCl}\) 432 kJ/mol
   
   Hint: \(\text{436 + 243 - 2x432}\)
   
   **Discussion** - If you are given the heat of the reaction, and the \(\ce{H-H}\) bond energy, can you calculate the bond energy for \(\ce{Cl-Cl}\)?

3. **Calculate the enthalpy of formation for** \(\ce{NH3}\).
   
   **Bond energies:** \(\ce{H2}\) 436 kJ/mol, \(\ce{N2}\) 945, \(\ce{H-N}\) 391 kJ/mol
   
   Hint: \(\text{3x436\{2\} + \frac{945\{2\}}{2} - 3\times391}\)
   
   **Another method** -
Writing the enthalpies of formation below their formulas in the equation, we have:
\[
\begin{alignat}{2}
\dfrac{3}{2} \ce{H2} &+ \dfrac{1}{2} \ce{N2} \rightarrow \ce{NH3} \\
\dfrac{3\times436}{2} &+ \dfrac{945}{2} = 3\times391 + H_\text{f}
\end{alignat}
\]

From this equation, we have:
\[
\text{\( H_f = \dfrac{3\times436}{2} + \dfrac{945}{2} - 3\times391 = -46.5 \text{ kJ/mol} \)}
\]

A handbook gives the enthalpy of formation of \( \ce{NH3} \) as -46.1 kJ/mol. As an exercise, use this value to calculate the triple bond energy of \( \ce{N2} \).

4. **Calculate the enthalpy of the reaction**

\[
\ce{CH4 + 2 O2 \rightarrow CO2 + 2 H2O)}
\]

from the enthalpies of formation: \( \ce{CH4} \) -75 kJ/mol, \( \ce{CO2} \) -394, and \( \ce{H2O_{(l)}} \) -286 kJ/mol.

Hint: -891 kJ

**Discussion** - The value calculated is the enthalpy of combustion of methane

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**Contributors**

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