HEAT OF FORMATION - HEAT OF DECOMPOSITION EQUATIONS

The standard heat of formation (\(\Delta H_f\)) of a compound is the change in enthalpy (heat content) that accompanies the formation of one mole of a substance from its elements with all of the substances in their standard states at 25°C.

EXAMPLE
The formation of one mole of potassium chlorate (\(\text{KClO}_3(s)\)).

\[ 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \rightarrow 1 \text{ KClO}_3(s) \]

The heat of formation of \(\text{KClO}_3(s)\) given in the data booklet was -397.7 kJ/mol. The negative sign indicated that the reaction was exothermic. When the elements combined to form the compound, \(\text{KClO}_3(s)\), energy was released to the surroundings. This energy can be expressed in the equation in two ways.

Method 1. Energy as a part of the equation

\[ 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \rightarrow 1 \text{ KClO}_3(s) + 397.7 \text{ kJ} \]

Method 2. Energy shown in the \(\Delta H\) notation

\[ 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \rightarrow 1 \text{ KClO}_3(s) \quad \Delta H_f = -397.7 \text{ kJ} \]

The standard heat of decomposition (\(\Delta H_{\text{decomposi}}\)) of a compound is the change in enthalpy (heat content) that accompanies the decomposition of one mole of a compound into the elements that originally formed it.

EXAMPLE
The decomposition of one mole of potassium chlorate (\(\text{KClO}_3(s)\)).

\[ 1 \text{ KClO}_3(s) \rightarrow 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \]

The heat of formation of \(\text{KClO}_3(s)\) was -397.7 kJ/mol. The heat of decomposition will be the same value given in the table of heats of formation; however, the sign will be reversed.

Method 1. Energy as a part of the equation

\[ 397.7 \text{ kJ} + 1 \text{ KClO}_3(s) \rightarrow 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \]

Method 2. Energy shown in the \(\Delta H\) notation

\[ 1 \text{ KClO}_3(s) \rightarrow 1 \text{ K}(s) + \frac{1}{2} \text{ Cl}_2(g) + 3/2 \text{ O}_2(g) \quad \Delta H_{\text{decomp}} = 397.7 \text{ kJ} \]
CALCULATIONS OF THE HEAT OF REACTION
BY THE USE OF HEATS OF FORMATION

Hess’s Law of Additivity states that a series of equations can be added in order to obtain an overall reaction, and if this is true, then the respective Heats of Formation for the reactions can be algebraically added.

**METHOD 1**

The overall enthalpy change for a chemical reaction is equal to the sum of the Heats of Formation of the products in the reaction minus the sum of Heats of Formation of the reactants.

\[ \Delta H_{\text{rxn}} = \sum n \Delta H_f^p - \sum n \Delta H_f^r \]

The example calculation will be for the combustion of a hydrocarbon (an organic molecule containing carbon and hydrogen atoms). Combustion is defined as the reaction of a substance with oxygen. If that substance is a hydrocarbon or a carbohydrate (an organic molecule containing carbon, hydrogen and oxygen), and if combustion is complete, then the products formed will be carbon dioxide gas and water vapor. Assume water to be gaseous unless the question stated differently.

**EXAMPLE CALCULATION**

Using the standard heats of formation in the Chemistry Data Booklet, calculate the molar heat of combustion of ethane (forming carbon dioxide gas and water vapor).

Step 1. Balance the equation (use the Chemistry Data Booklet).

\[ \text{C}_2\text{H}_6(g) + \frac{7}{2} \text{O}_2(g) \rightarrow 2 \text{CO}_2(g) + 3 \text{H}_2\text{O}(g) \]

Step 2. Define the formula to be used in the calculation.

\[ \Delta H_{\text{rxn}} = \sum n \Delta H_f^p - \sum n \Delta H_f^r \]

Step 3. Substitute values for heats of formation into the formula.

\[ \Delta H_{\text{rxn}} = [\sum n \Delta H_f^p - \sum n \Delta H_f^r] \]

\[ \Delta H_{\text{rxn}} = [\{(2 \text{ mol}) \cdot (-393.5 \text{ kJ/mol}) + (3 \text{ mol}) \cdot (-241.8 \text{ kJ/mol})\} - \{(1 \text{ mol}) \cdot (-84.7 \text{ kJ/mol})\}] \]

\[ = \{(-787 \text{ kJ}) + (-725.4 \text{ kJ})\} - (-84.7 \text{ kJ}) \]

\[ = -1512.4 \text{ kJ} + 84.7 \text{ kJ} \]

\[ = -1427.7 \text{ kJ} \]

The calculation in the problem was for one mole of ethane; therefore, the molar heat of combustion of ethane was -1427.7 kJ.
HESS'S LAW - CALCULATIONS

METHOD 2

Hess's Law of Additivity employs the actual addition of equations in order to arrive at the required reaction.

EXAMPLE CALCULATION

Using Hess’s Law of Additivity and the following equations, determine the molar heat of combustion for cyclopentane, C₅H₁₀(0).

(a) 5 C(0) + 5 H₂(g) → C₅H₁₀(0) \( \Delta H = -77.2 \text{ kJ} \)
(b) C(0) + O₂(g) → CO₂(g) \( \Delta H = -393.5 \text{ kJ} \)
(c) H₂(g) + ½ O₂(g) → H₂O(g) \( \Delta H = -241.8 \text{ kJ} \)

Step 1. Write the balanced equation for the combustion of one mole of cyclopentane, C₅H₁₀(0).

\[ C₅H₁₀(0) + 15/2 O₂(0) \rightarrow 5 CO₂(0) + 5 H₂O(0) \]

Step 2. The three equations given in the data must be added in order to obtain the required balanced equation given in Step 1. C₅H₁₀(0) is given as a reactant in the required equation in Step 1. The equation requires one mole of C₅H₁₀(0). Equation (a) has the C₅H₁₀(0) as a product; therefore, the equation must be reversed. When the equation is reversed, the sign on the \( \Delta H \) changes. The 15/2 O₂ shown as the next term in the required equation has a \( \Delta H = 0 \); therefore it will not appear in the calculations.

Five moles of CO₂(g) are required in equation (b) and the CO₂(g) must be a product. Multiply every term in the equation by 5.

Five moles of H₂O(g) are required in equation (c) and the H₂O(g) must be a product. Multiply every term in the equation by 5.

Add the three equations.

\[ (a) \ C₅H₁₀(0) \rightarrow 5 C(0) + 5 H₂(g) \quad \Delta H = 77.2 \text{ kJ} \]
\[ (b) \ 5 C(0) + 5 O₂(g) \rightarrow 5 CO₂(g) \quad \Delta H = (5)(-393.5 \text{ kJ}) \]
\[ (c) \ 5 H₂(g) + 5/2 O₂(g) \rightarrow 5 H₂O(g) \quad \Delta H = (5)(-241.8 \text{ kJ}) \]

\[ C₅H₁₀(0) + 15/2 O₂(0) \rightarrow 5 CO₂(0) + 5 H₂O(0) \quad \Delta H = -3099.3 \text{ kJ} \]
\[ \Delta H = -3.10 \times 10³ \text{ kJ} \]

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CALORIMETRY

METHOD 3

Calorimetry is the process that is used to measure energy transfers which occur in isolated systems when one substance loses energy and another substance gains that energy.

\[
\text{Heat Lost} = \text{Heat Gained}
\]

This transfer of energy can be measured from experimental data obtained by using calorimeters. The calculations in the calorimetry section are all based upon the Law of Conservation of Energy. Whenever calorimetry experiments are carried out in the laboratory, the following assumptions are made:

- heat is not transferred between the calorimeter and the surroundings.
- dilute, aqueous solutions are considered to have the same density and specific heat capacity as water.
- negligible heat energy was absorbed by the polystyrene calorimeters, the stirring rod or the thermometer.

EXAMPLE CALCULATION

A heat transfer of 9.73 kJ would be required to raise the temperature of a calorimeter and its contents by 1.00°C. When 3.73 g of benzene, C₆H₆, were burned as the heat source, the temperature of the calorimeter and its contents was increased by 15.0°C. Calculate the heat of combustion for one mole of benzene. Separate the data according to heat lost and heat gained.

\[
\begin{align*}
\text{HEAT LOST} & = \text{HEAT GAINED} \\
\text{Benzene} & \quad \text{Calorimeter and Contents} \\
3.73 \text{ g} & \quad \text{C} = 9.73 \text{ kJ/g°C} \\
\text{Molar Mass} = 78.12 \text{ g/mol} & \quad \Delta T = 15.0°C
\end{align*}
\]

FORMULA

\[ n \, \text{H} = C \, \Delta T \]

SUBSTITUTING IN FORMULA

\[
\begin{align*}
3.73 \text{ g} \quad (\text{H}) & = \quad (9.73 \text{ kJ/°C}) \quad (15.0°C) \\
78.12 \text{ g/mol} & \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad H_{\text{combustion}} = -3056.732976 \text{ kJ/mol} \\
& \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad \quad H_{\text{combustion}} = -3.10 \times 10^3 \text{ kJ/mol}
\end{align*}
\]

WIST: Hess's Law - Calorimetry

The heat of combustion for one mole of benzene was -3.10 x 10³ kJ/mol.