Enthalpy of Chemical Reactions

Out main interest here is to apply the first law of thermodynamics to chemical reactions carried out under certain conditions. These conditions are constant volume and constant pressure. This is because when we carry out the experiment in the laboratory, we usually work with definite volume (constant volume) of reaction. In addition, the pressure inside the laboratory is pretty much the same as the atmospheric pressure, which is constant (constant pressure). Thus we have two different kinds of quantities, ΔE and ΔH, to measure the energy changes one at constant volume (ΔE) and another at constant pressure (ΔH). Both are thermodynamic state functions; ΔE is known as the change in internal energy and ΔH is labeled as the change in enthalpy (from Greek, *enthalpein*, to warm).

Remember, the word enthalpy is simply a fancy word for heat at constant pressure**.**

Enthalpy Change in Reactions

Since most of the chemical reactions in laboratory are nothing but the constant-pressure processes, we can write the change in enthalpy (also known as enthalpy of reaction) for a reaction. Consider the following general type of reaction

reactant → products

The ΔH is defined as the difference between the enthalpies of products and the reactants. Thus

$$\Delta H = H_{products} - H_{reactants}$$

The enthalpy of reaction can be positive or negative or zero depending upon whether the heat is gained or lost or no heat is lost or gained:

$\Delta H > 0$,　　　　if $H_{products} > H_{reactants}$　　endothermic reaction (ΔH is positive (+))

$\Delta H < 0$,　　　　if $H_{products} < H_{reactants}$,　　exothermic reaction　($\Delta H$ is negative (-))

$\Delta H = 0$,　　　　if $H_{products} = H_{reactants}$,　　no heat is lost or gained (ΔH is zero)

Thermochemical Equations

When we write chemical equations to represent chemical reactions, we simply write the balanced chemical equations. However, within the realm of the thermodynamics, we must write the chemical equations with change in heat (enthalpy change). Such equations are known as **thermochemical equations.** Consider the process of melting the ice, for which we write the following chemical equation:

H_2O (s) → H_2O (l)
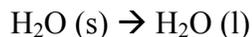
This equation simply says that one mole of ice melts and one mole of water forms. But in reality, the melting process involves absorption of certain amount of heat by the ice. Now we have to incorporate that heat as a part of the chemical reaction that is indicated by the enthalpy change. When you do that it becomes a thermochemical equation.

$$H_2O \ (s) \rightarrow H_2O \ (l) \qquad \qquad \Delta H = 6.01 \ kJ/mol$$
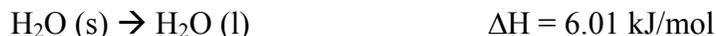
First of all, the ΔH is positive ($\Delta H > 0$) because it is an endothermic reaction (heat is absorbed by the ice from the surrounding), and secondly, ΔH is written per mole of reaction. In this example, 1 mole of ice is converted to 1mole of water.

As another example, consider the oxidation of graphite to produce carbon dioxide gas:

$$C \ (graphite) + O_2 \ (g) \rightarrow CO_2 \ (g) \qquad \Delta H = - \ 393.5 \ kJ/mol$$
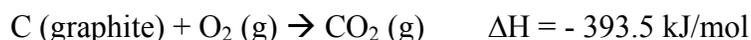
Here the ΔH is negative ($\Delta H < 0$) because it is an exothermic reaction. It means that when 1 mole of graphite is burned, 393.5 kJ heat is liberated to the surrounding.

The above written equations for the melting of ice and oxidation of graphite are examples of **thermochemical equations** that show mass relationship as well as enthalpy change. There are certain properties of thermochemical equations that you should know:

1. You must always specify the physical state of all reactants and products because it helps to determine the actual enthalpy change. As you know the chemical formula for water is H_2O whether it is in solid state (ice) or liquid state (water) or gaseous state (vapor). However, the amount of energy involved going from one state to another state is not the same. The above mentioned 6.01 kJ refers to the enthalpy change going from the solid state to the liquid sate only.

2. If we multiply both sides of the thermochemical equation by a certain number, then the ΔH must also be multiplied by the same number. Thus if we multiply the melting of ice equation by 2, then we also have to multiply the ΔH by 2.

$$2H_2O \ (s) \rightarrow 2H_2O \ (l) \qquad \Delta H = 2 \ x \ 6.01 \ kJ/mol = 12.02 \ kJ/mol$$
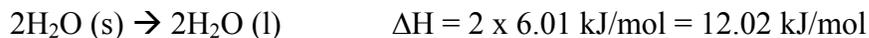
3. When we reverse the thermochemical equation, we make the reactants to become products and products to become reactants. In that case, the sign on ΔH must be reversed without changing the magnitude of ΔH. For examples, freezing of water to ice is represented by

$$H_2O \ (l) \rightarrow H_2O \ (s) \qquad \qquad \Delta H = - \ 6.01 \ kJ/mol$$
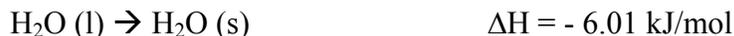
This now becomes an exothermic reaction. This makes sense because when the ice is formed the heat is released (lost) to the surrounding by the water. If the water does not lose the heat, it will not become an ice.

Example-1

Consider the reaction

$$H_2 \text{ (g)} + Cl_2 \text{ (g)} \rightarrow 2HCl \text{ (g)} \qquad \Delta H = -184.6 \text{ kJ/mol}$$
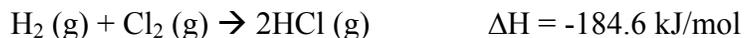
What is the value of ΔH if (a) the equation is multiplied throughout by 3, and (b) the direction of the reaction is reversed so that the products become the reactants and vice versa.

Answer-1

(a) When you multiply the equation by 3, the ΔH must also be multiplied by 3. Thus

$$3H_2 \text{ (g)} + 3Cl_2 \text{ (g)} \rightarrow 6HCl \text{ (g)} \qquad \Delta H = 3 \text{ x } -184.6 \text{ kJ/mol} = - 553.8 \text{ kJ}$$

(b) If the direction of reaction is reversed, the sign on ΔH is reversed without changing the magnitude. Thus

$$2HCl \text{ (g)} \rightarrow H_2 \text{ (g)} + Cl_2 \text{ (g)} \qquad \Delta H = 184.6 \text{ kJ/mol}$$

 Example-2

Given the following thermochemical equation

$$CH_4 \text{ (g)} + 2O_2 \text{ (g)} \rightarrow CO_2 \text{ (g)} + 2H_2O \text{ (l)} \qquad \Delta H = -890.4 \text{ kJ/mol}$$
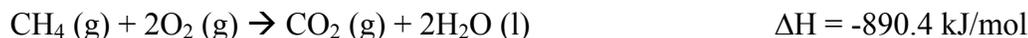
calculate the heat evolved when 20 g of CH_4 is converted to CO_2 (g) and H_2O(l).

Answer-2

The chemical equations are always written in terms of moles, but problem is stated in terms of mass. You need to relate mole to mass through molar mass (mole = mass / molar mass). There are two ways of doing this problem; both should yield the same result.

    1.   moles of $CH_4 \rightarrow$ grams of $CH_4 \rightarrow$ kilojoules of heat

    2.   grams of $CH_4 \rightarrow$ moles of $CH_4 \rightarrow$ kilojoules of heat

First Method:

First calculate the mass of one mole of CH_4, which is 16 g/mol. Then set up the ratio to calculate the heat produced by 20 g of CH_4.

$$20g \, CH_4 x \frac{1mol \, CH_4}{16g \, CH_4} x \frac{-890.4kJ}{1mole \, CH_4} = -1113.0kJ$$

Second Method:

First convert 20 g of CH_4 to moles of CH_4, that is

$$mol\ CH_4 = \frac{20g\ CH_4}{16g\ CH_4} = 1.35\ mol\ CH_4$$

Then, set up the ratio to calculate the heat produced by 1.25 mol of CH_4.

$$1.25\ mol\ CH_4 x \frac{-890.4kJ}{1mol\ CH_4} = -1113.0kJ$$

Notice the similarity between both setups. The factor, $20g\ CH_4 x \frac{1mol\ CH_4}{16g\ CH_4}$, in the first method is nothing but 1.25 mol CH_4.