Hess's Law

Since enthalpy is a state function, the change in enthalpy in going from some initial state to some final state is independent of the pathway. **Hess's law** state that the change in enthalpy (ΔH) in going from a particular set of reactants to a particular set of products is the same regardless of the number of steps the reactions take.

For example, when nitrogen gas is completely burned to NO_2 , $\Delta H^0 = 68$ kJ/mol nitrogen.

1.
$$N_{2(q)} + 2 O_{2(q)} \rightarrow 2 NO_{2(q)}; \Delta H^{0}_{(1)} = 68 \text{ kJ}$$

If nitrogen is converted to NO and the nitrogen monoxide is then converted to NO₂, the total amount of heat absorbed is also equal to 68 kJ:

2.
$$N_{2(q)} + O_{2(q)} \rightarrow 2NO_{(q)};$$
 $\Delta H^{0}_{(2)} = 180 \text{ kJ}$

3.
$$2NO_{(g)} + O_{2(g)} \rightarrow 2NO_{2(g)};$$
 $\Delta H^{0}_{(3)} = -112 \text{ kJ}$

Net reaction:
$$N_{2(g)} + 2 O_{2(g)} \rightarrow 2 NO_{2(g)};$$
 $\Delta H^{o}_{net} = \Delta H^{o}_{(2)} + \Delta H^{o}_{(3)} = 68 \text{ kJ}$

Thus, if reaction(1) + reaction(2) = reaction(3), then $\Delta H_{(1)} + \Delta H_{(2)} = \Delta H_{(3)}$; where $\Delta H_{(1)}$, $\Delta H_{(2)}$ and $\Delta H_{(3)}$ are enthalpy changes for reaction(1), reaction(2), and reaction(3), respectively.

According to the Hess's law, if two or more reactions can be combined to produce an overall reaction, then the enthalpy of the overall reaction is equal to the sum of the enthalpy of individual reactions.

Hess's law can be used to calculate the enthalpy of a particular reaction in a series of reactions for which the enthalpy of the net reaction and those of the other reactions in the series are known. Hess's Law is useful for calculating the enthalpy of reactions, which cannot be measured directly. For instance, the enthalpy of formation of carbon monoxide, CO, cannot be obtained experimentally because when carbon is burned in a limited oxygen supply, the product will always be a mixture of CO and CO_2 . On the other hand, the enthalpy for the complete combustion of carbon to CO_2 and for the reaction to convert CO to CO_2 can be experimentally measured with a bomb-calorimeter. For example:

1.
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};$$
 $\Delta H^{o}_{(1)} = -394 \text{ kJ}$

2.
$$CO_{(g)} + \frac{1}{2}O_{2(g)} \rightarrow CO_{2(g)};$$
 $\Delta H^{0}_{(2)} = -283 \text{ kJ}$

If we subtract equation (1) with equation (2), we obtain equation(3) and its enthalpy change:

3.
$$C_{(s)} + \frac{1}{2} O_{2(g)} \rightarrow CO_{(g)};$$
 $\Delta H^{o}_{(3)} = -111 \text{ kJ}$
$$(\Delta H^{o}_{(3)} = \Delta H^{o}_{(1)} - \Delta H^{o}_{(2)} = -394 \text{ kJ} - (-283 \text{ kJ}) = -111 \text{ kJ})$$

Note that:

- 1. If the reaction is reverse, the sign of ΔH is also reversed ("+" \rightarrow "-"; "-" \rightarrow "+")
- 2. The magnitude of ΔH is directly proportional to the quantity of reactants and products. If the coefficients in a balanced equation are multiplied by an integer, the numerical value of ΔH is also multiplied by the same factor.

3. In a given reaction, the quantity of heat produced or absorbed is proportional to the molar amount of the limiting reactant.

For example:
$$H_{2(g)} + \frac{1}{2}O_{2(g)} \rightarrow H_2O_{(l)};$$
 $\Delta H^o = -286 \text{ kJ}$
 $2 H_{2(g)} + O_{2(g)} \rightarrow 2 H_2O_{(l)};$ $\Delta H^o = 2(-286 \text{ kJ}) = -572 \text{ kJ}$
 $C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};$ $\Delta H^o = -394 \text{ kJ}$
 $2C_{(s)} + 2 O_{2(g)} \rightarrow 2CO_2(g);$ $\Delta H^o = 2(-394 \text{ kJ}) = 788 \text{ kJ}$

Exercise

1. The enthalpy changes for the combustion of ethane (C_2H_6) , carbon, and hydrogen are given below:

(1)
$$C_2H_{6(g)} + {}^7/_2 O_{2(g)} \rightarrow 2 CO_{2(g)} + 3 H_2O_{(l)}; \quad \Delta H^{\circ}_{(1)} = -1560 \text{ kJ}$$

(2)
$$C_{(s)} + O_{2(g)} \rightarrow CO_{2(g)};$$
 $\Delta H^{0}_{(2)} = -394 \text{ kJ}$

(3)
$$H_{2(q)} + \frac{1}{2} O_{2(q)} \rightarrow H_2 O_{(l)};$$
 $\Delta H^0_{(3)} = -286 \text{ kJ}$

Calculate the enthalpy change for the formation of ethane (C_2H_6) according to the equation below:

$$2 C_{(s)} + 3 H_{2(g)} \rightarrow C_2 H_{6(g)}; \qquad \Delta H_f = ?$$

2. Calculate ΔH for the synthesis of diborane (B₂H₆) from its elements, according to the equation:

$$2B_{(s)} + 3 H_{2(g)} \rightarrow B_2 H_{6(g)}$$

using the following data:

(1)
$$2B_{(s)} + {}^{3}/_{2} O_{2(a)} \rightarrow B_{2}O_{3(s)};$$
 $\Delta H_{(1)} = -1273 \text{ kJ};$

(2)
$$B_2H_{6(g)} + 3 O_{2(g)} \rightarrow B_2O_{3(s)} + 3H_2O_{(g)};$$
 $\Delta H_{(2)} = -2035 \text{ kJ};$

(3)
$$H_{2(g)} + \frac{1}{2} O_{2(g)} \rightarrow H_2O_{(g)};$$
 $\Delta H_{(3)} = -242 \text{ kJ}$