Hess's Law

Chapter 5.4

Enthalpies of Reaction

- For a reaction:

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

- Enthalpy is an *extensive* property (magnitude ΔH is directly proportional to amount):

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ ΔH = -802 kJ

$2CH_4(g) + 4O_2(g) \rightarrow 2CO_2(g) + 4H_2O(g)$ ΔH = -1604 kJ

Hess's Law of Constant Heat Summation

- Some reactions cannot be carried out "as written."
- Consider the reaction:

  C(graphite) + ½ O_2(g) → CO(g).
- If we burned 1 mol C in ½ mol O_2, both CO and CO_2 would probably form. Some C might be left over. However …

Hess's Law of Constant Heat Summation

- … enthalpy change is a *state function.*
- The enthalpy change of a reaction is the *same* whether the reaction is carried out in one step or through a number of steps.

Hess's Law

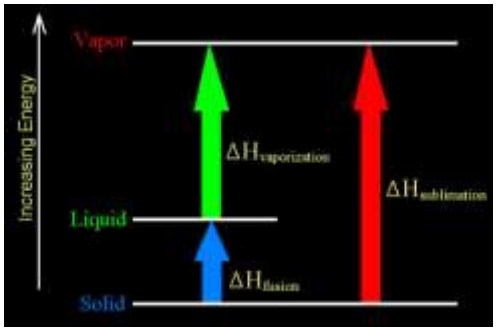
G. H. Hess

- In going from a particular set of reactants to a particular set of products, the enthalpy change is the same whether the reaction takes place in one step or in a series of steps.
- It is often possible to calculate ΔH for a reaction from listed ΔH values of other reactions (i.e. you can avoid having to do an experiment)

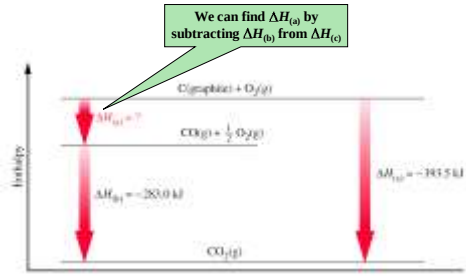
Characteristics of Enthalpy Changes

- If a reaction is reversed, the sign of ΔH is also reversed.
- If the coefficients in a balanced reaction are multiplied by an integer, the value of ΔH is multiplied by the same integer.

Hess Energy Diagram



Hess's Law: An Enthalpy Diagram



Application of Hess' Law

Consider the combustion of methane to form CO_2 and liquid H_2O

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$$

This reaction can be thought of as occurring in two steps

In the first step methane is combusted to produce water vapor:

$$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$$

In the second step water vapor condenses from the gas phase to the liquid phase:

$$2H_2O(g) \rightarrow 2H_2O(l)$$

Question 1

What is the heat of reaction for the combustion of methane to form liquid water and carbon dioxide?

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(g)$ $\Delta H = -802$ kJ

$2H_2O(g) \rightarrow 2H_2O(l)$ $\Delta H = -88$ kJ

Combining these equations yields the following:

$CH_4(g) + 2O_2(g) + 2H_2O(g) \rightarrow CO_2(g) + 2H_2O(g) + 2H_2O(l)$

$CH_4(g) + 2O_2(g) \rightarrow CO_2(g) + 2H_2O(l)$

$\Delta H = (-802)$ kJ + (-88) kJ$= -890$ kJ

Hess's Law: if a reaction is carried out in a series of steps, ΔH for the reaction will be equal to the sum of the enthalpy changes for the individual steps

Question 2

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H = ?$

$3\,C(s) + 4\,H_2(g) \rightarrow C_3H_8(g)$ $\Delta H = -103.85$kJ/mol

$C(s) + O_2(g) \rightarrow CO_2(g)$ $\Delta H = -393.51$kJ/mol

$H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)$ $\Delta H = -241.83$kJ/mol

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H = ?$

$C_3H_8(g) \rightarrow 3\,C(s) + 4\,H_2(g)$ $\Delta H = +103.85$kJ/mol

$3[C(s) + O_2(g) \rightarrow CO_2(g)]$ $3[\Delta H = -393.51$kJ/mol$]$

$4[H_2(g) + \frac{1}{2} O_2(g) \rightarrow H_2O(g)]$ $4[\Delta H = -241.83$kJ/mol$]$

$C_3H_8(g) + 5O_2(g) \rightarrow 3CO_2(g) + 4H_2O(g)$ $\Delta H = -2044.00$kJ/mol

Calculate the standard enthalpy of formation of CS_2 (*l*) given that:

$C_{(graphite)} + O_2\ (g) \longrightarrow CO_2\ (g)$ $\quad \Delta H^0_{rxn} = -393.5$ kJ

$S_{(rhombic)} + O_2\ (g) \longrightarrow SO_2\ (g)$ $\quad \Delta H^0_{rxn} = -296.1$ kJ

$CS_2(l) + 3O_2\ (g) \longrightarrow CO_2\ (g) + 2SO_2\ (g)$ $\quad \Delta H^0_{rxn} = -1072$ kJ

1. Write the enthalpy of formation reaction for CS_2

$$C_{(graphite)} + 2S_{(rhombic)} \longrightarrow CS_2\ (l)$$

2. Add the given rxns so that the result is the desired rxn.

$C_{(graphite)} + O_2\ (g) \longrightarrow CO_2\ (g)$ $\quad \Delta H^0_{rxn} = -393.5$ kJ

$2S_{(rhombic)} + 2O_2\ (g) \longrightarrow 2SO_2\ (g)$ $\quad \Delta H^0_{rxn} = -296.1 \times 2$ kJ

\+ $CO_2(g) + 2SO_2\ (g) \longrightarrow CS_2\ (l) + 3O_2\ (g)$ $\quad \Delta H^0_{rxn} = +1072$ kJ

$C_{(graphite)} + 2S_{(rhombic)} \longrightarrow CS_2\ (l)$

$\Delta H^0_{rxn} = -393.5 + (2x\text{-}296.1) + 1072 = 86.3$ kJ