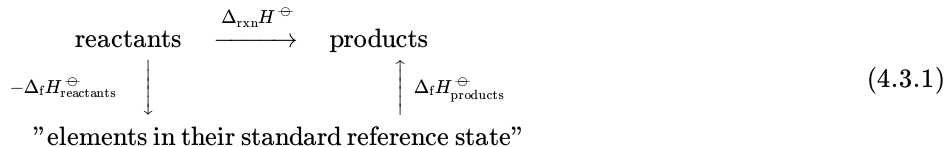


## 4.3: Hess's Law

The calculation of a standard reaction enthalpy can be performed using the following cycle:



This process is summarized by the simple formula:

$$\Delta_{\text{rxn}} H^{\ominus} = \Delta_f H_{\text{products}}^{\ominus} - \Delta_f H_{\text{reactants}}^{\ominus} \quad (4.3.2)$$

Notice how there is a negative sign in front of the enthalpy of formation of the reactants because they are normally defined for the reactions that go from the elements to the reactants and not vice-versa. To close the cycle in Equation 4.3.1, however, we should go from the reactants to the elements, and therefore we must invert the sign in front of the formation enthalpies of the reactants. Equation 4.3.2 can be generalized using the same technique used to derive eq. 4.1.4, resulting in:

$$\Delta_{\text{rxn}} H^{\ominus} = \sum_i \nu_i \Delta_f H_i^{\ominus}, \quad (4.3.3)$$

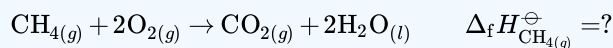
which is a mathematical expression of the law that is known as **Hess's Law**. Hess's law is valid at constant pressure because, at those conditions, the heat of reaction—a path function—is equal to the enthalpy of reaction—a state function. Therefore, the enthalpy of a reaction depends exclusively on the initial and final state, and it can be obtained via the pathway that passes through the elements in their standard state (the formation pathway).

### ? Exercise 4.3.1

Calculate the standard enthalpy of formation at 298 K for the combustion of 1 mol of methane, using the data in eq. 4.2.1.

#### Answer

The reaction that is under consideration is:



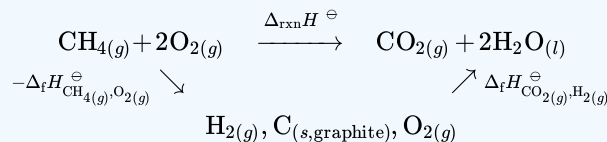
Using Hess's Law, Equation 4.3.3 the enthalpy of formation for methane is:

$$\Delta_{\text{rxn}} H^{\ominus} = \Delta_f H_{\text{CO}_2(g)}^{\ominus} + 2\Delta_f H_{\text{H}_2\text{O}_{(l)}}^{\ominus} - \Delta_f H_{\text{CH}_4(g)}^{\ominus} - \underbrace{2\Delta_f H_{\text{O}_{2(g)}}^{\ominus}}_{=0}$$

whose values are reported in eq. 4.2.1. Notice that the formation enthalpy of  $\text{O}_{2(g)}$  is zero, since it is an element in its standard state. The final result is:

$$\Delta_{\text{rxn}} H^{\ominus} = \underbrace{\Delta_f H_{\text{CO}_2(g)}^{\ominus}}_{-394} + 2 \underbrace{\Delta_f H_{\text{H}_2\text{O}_{(l)}}^{\ominus}}_{(-286)} - \underbrace{\Delta_f H_{\text{CH}_4(g)}^{\ominus}}_{(-75)} = -891 \text{ kJ/mol.}$$

where the negative sign indicates that the reaction is exothermic (see eq. 4.1.1), as we should expect. The cycle that we used to solve this exercise can be summarized with :



Notice that at standard pressure and  $T = 298 \text{ K}$  water is in liquid form. However, when we burn methane, the heat associated with the exothermic reaction immediately vaporize the water. Substances in different states of matter have different formation enthalpies, and  $\Delta_f H_{\text{H}_2\text{O}_{(l)}}^{\ominus} = -242 \text{ kJ/mol}$ . The difference between the formation enthalpies of the same substance in different states represents the latent heat that separates them. For example, for water:

$$\begin{aligned}\Delta_{\text{vap}}H_{\text{H}_2\text{O}}^{\ominus} &= \Delta_{\text{f}}H_{\text{H}_2\text{O}(\text{g})}^{\ominus} - \Delta_{\text{f}}H_{\text{H}_2\text{O}(\text{l})}^{\ominus} \\ &= (-242) - (-286) = +44 \text{ kJ/mol}\end{aligned}$$

which is the latent heat of vaporization for water,  $\Delta_{\text{vap}}H_{\text{H}_2\text{O}}^{\ominus}$ . The latent heat is positive to indicate that the system absorbs energy in going from the liquid to the gaseous state (and it will release energy when going the opposite direction from gas to liquid).

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