

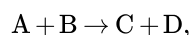
4.1: Reaction Enthalpies

In [chapter 3](#), we have discussed thermodynamical changes in energy in the absence of chemical reactions. When a chemical reaction takes place, some bonds break and/or some new one form. This process either absorbs or releases the energy contained in these bonds. For a proper thermodynamic treatment of the system, this extra energy must be included in the net balance.

In this chapter, we will consider the heat associated with chemical reactions. Since most chemical reactions happen at constant atmospheric pressure (isobaric conditions) in the lab, we can use [eq. 3.1.13](#) to replace the inexact differential of the heat with the exact differential of the state function called enthalpy. The advantage of this transformation is that it allows us to study the heat associated with chemical reactions at constant pressure independently of their path. If we call the molecules at the beginning of the reaction “reactants” and the molecules at the end of the reaction “products,” the heat associated with the reaction (rxn) is defined as:

$$\Delta_{\text{rxn}}H = H_{\text{products}} - H_{\text{reactants}} .$$

For example, if we take a simple reaction of the form:



the heat at constant pressure is equal to the enthalpy of reaction, which is calculated as:

$$Q_P = \Delta_{\text{rxn}}H = \underbrace{(H_C + H_D)}_{\text{products}} - \underbrace{(H_A + H_B)}_{\text{reactants}} . \quad (4.1.1)$$

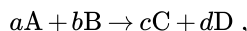
Using the chemistry sign convention, [Definition: System-centric](#), reactions are classified in terms of the sign of their reaction enthalpies as follows:

Definition: Signs of Reaction Enthalpies

$\Delta_{\text{rxn}}H > 0 \Rightarrow$ Endothermic reaction (heat is gained by the system).

$\Delta_{\text{rxn}}H < 0 \Rightarrow$ Exothermic reaction (heat is lost by the system).

If we expand the sample reaction to account for its stoichiometry:



where a, b, c, d are the stoichiometric coefficients of species A, B, C, D. Equation [4.1.1](#) can be rewritten as:

$$Q_P = \Delta_{\text{rxn}}H = \underbrace{(cH_C + dH_D)}_{\text{products}} - \underbrace{(aH_A + bH_B)}_{\text{reactants}} , \quad (4.1.2)$$

while for the most general case we can write it:

$$\Delta_{\text{rxn}}H = \sum_i \nu_i H_i ,$$

where ν_i is the stoichiometric coefficient of species i with its own sign. The signs of the stoichiometric are defined according to Equation [4.1.2](#) as:

Definition: Signs of the stoichiometric coefficients

ν_i is positive if i is a product.

ν_i is negative if i is a reactant.

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