5.4: The Effect of Temperature on Reaction Rates

In practice, rate constants vary in response to changes in several factors. Indeed, they are usually the same in two experiments only if we keep everything but the reagent concentrations the same. Another way of saying this is that the rate law captures the dependence of reaction rate on concentrations, while the dependence of reaction rate on any other variable appears as a dependence of rate constants on that variable.

Temperature usually has a big effect. The experimentally observed dependence of rate constants on temperature can be expressed in a compact fashion. Over small temperature ranges it can usually be expressed adequately by the ***Arrhenius equation***:

$$k = A \exp \left(\frac{-E_a}{RT} \right)$$

where E_a and A are called the ***Arrhenius activation energy*** and the ***frequency factor*** (or ***pre-exponential factor***), respectively.

The Arrhenius equation is an empirical relationship. As we see below for our collision-theory model, theoretical treatments predict that the pre-exponential term, A, is weakly temperature dependent. When we investigate reaction rates experimentally, the temperature dependence of A is usually obscured by the uncertainties in the measured rate constants. It is often said, as a rough rule of thumb, that the rate of a chemical reaction doubles if the temperature increases by 10 K. However, this rule can fail spectacularly. A reaction can even proceed more slowly at a higher temperature, and there are multi-step reactions for which this is observed.