

15.4: Temperature Dependence of the Rate Coefficients

The dependence of the rate coefficient, k , on the temperature is given by the **Arrhenius equation**. This formula was derived by Svante August Arrhenius (1859–1927) in 1889 and is based on the simple experimental observation that every chemical process gets faster when the temperature is increased. Working on data from equilibrium reactions previously reported by van 't Hoff, Arrhenius proposed the following simple exponential formula to explain the increase of k when T is increased:

$$k = A \exp\left(\frac{E_a}{RT}\right), \quad (15.4.1)$$

where A is the so-called Arrhenius pre-exponential factor, and E_a is the activation energy. Both of these terms are independent of temperature,¹ and they represent experimental quantities that are unique to each individual reaction. Since there is no known exception to the fact that a temperature increase speeds up chemical reactions, both A and E_a are always positive. The pre-exponential factor units are the same as the rate constant and will vary depending on the order of the reaction. As suggested by its name, the activation energy has units of energy per mole of substance, $\frac{\text{J}}{\text{mol}}$ in SI.

The Arrhenius equation is experimentally useful in its linearized form, which is obtained from two Arrhenius experiments, taken at different temperatures. Applying Equation 15.4.1 to two different experiments, and taking the ratio between the results, we obtain:

$$\ln \frac{k_{T_2}}{k_{T_1}} = -\frac{E_a}{RT} \left(\frac{1}{T_2} - \frac{1}{T_1} \right), \quad (15.4.2)$$

which gives the plot of Figure 15.4.1, from which E_a can be determined.

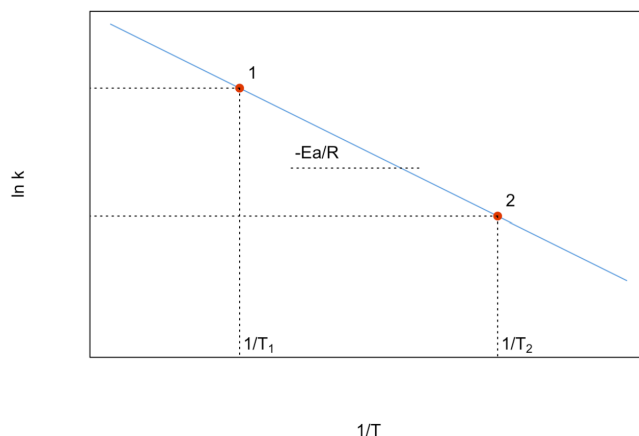


Figure 15.4.1: Arrhenius Plot Obtained Using Experimental Data at Two Different Temperatures.

From empirical arguments, Arrhenius proposed the idea that reactants must acquire a minimum amount of energy before they can form any product. He called this amount of minimum energy the activation energy. We can motivate this assumption by plotting energy of a reaction along the reaction coordinate, as in Figure 15.4.3² The reaction coordinate is defined as the minimum energy path that connects the reactants with the products.

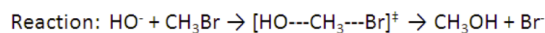
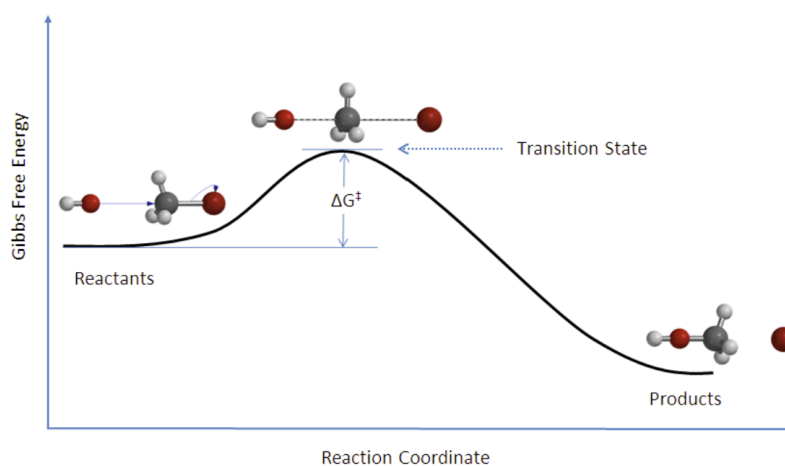


Figure 15.4.3: Reaction Coordinate Diagram for a Typical Reaction.

1. In theory, both A and E_a show a weak temperature dependence. However, they can be considered constants at most experimental conditions, since kinetic studies are usually performed in a small temperature range.
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