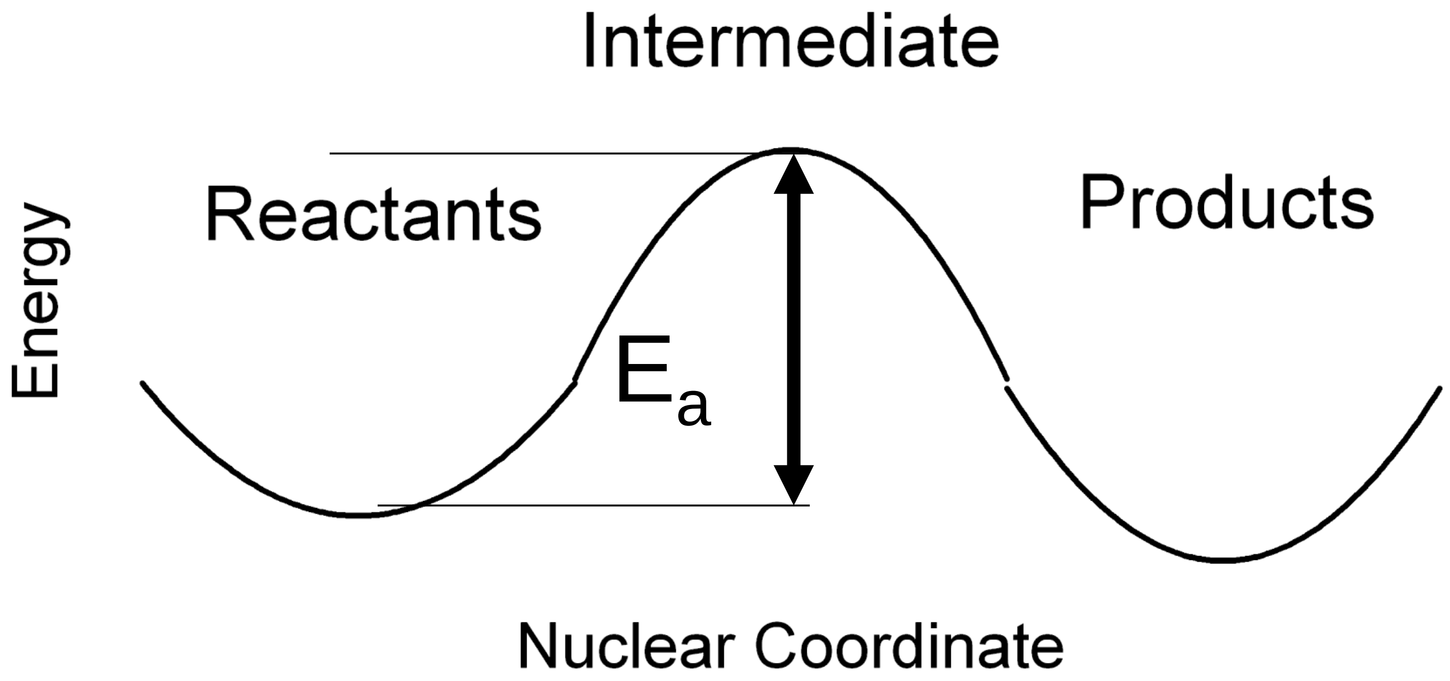
Activated complex theory



The diagram depicts a reaction coordinate.
The intermediate is the activated complex.

The Arrhenius equation

The Arrhenius model for the temperature dependence of the rate constant is:

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

A is the pre-exponential or frequency factor.

E_a is the activation energy.

Is this exponential dependence accidental?

No, it is not. We will see that the activation energy can be related to the enthalpies of the forward and reverse reactions.

Linearized Arrhenius equation

The empirical observation is that:

$$\ln(k) = \ln(A) - \frac{E_a}{RT}$$

for many reactions. This means that a plot of ln(k) vs. 1/T gives a straight line.
A is the intercept and $-E_a/R$ is the slope of the line. For example, if we take two rate constants at two temperatures we have:

$$\ln\left(\frac{k_2}{k_1}\right) = -\frac{E_a}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

Since we will not use least-squares fitting (to a line), The most common for for problems is the above form.

Experimental determination of Arrhenius parameters

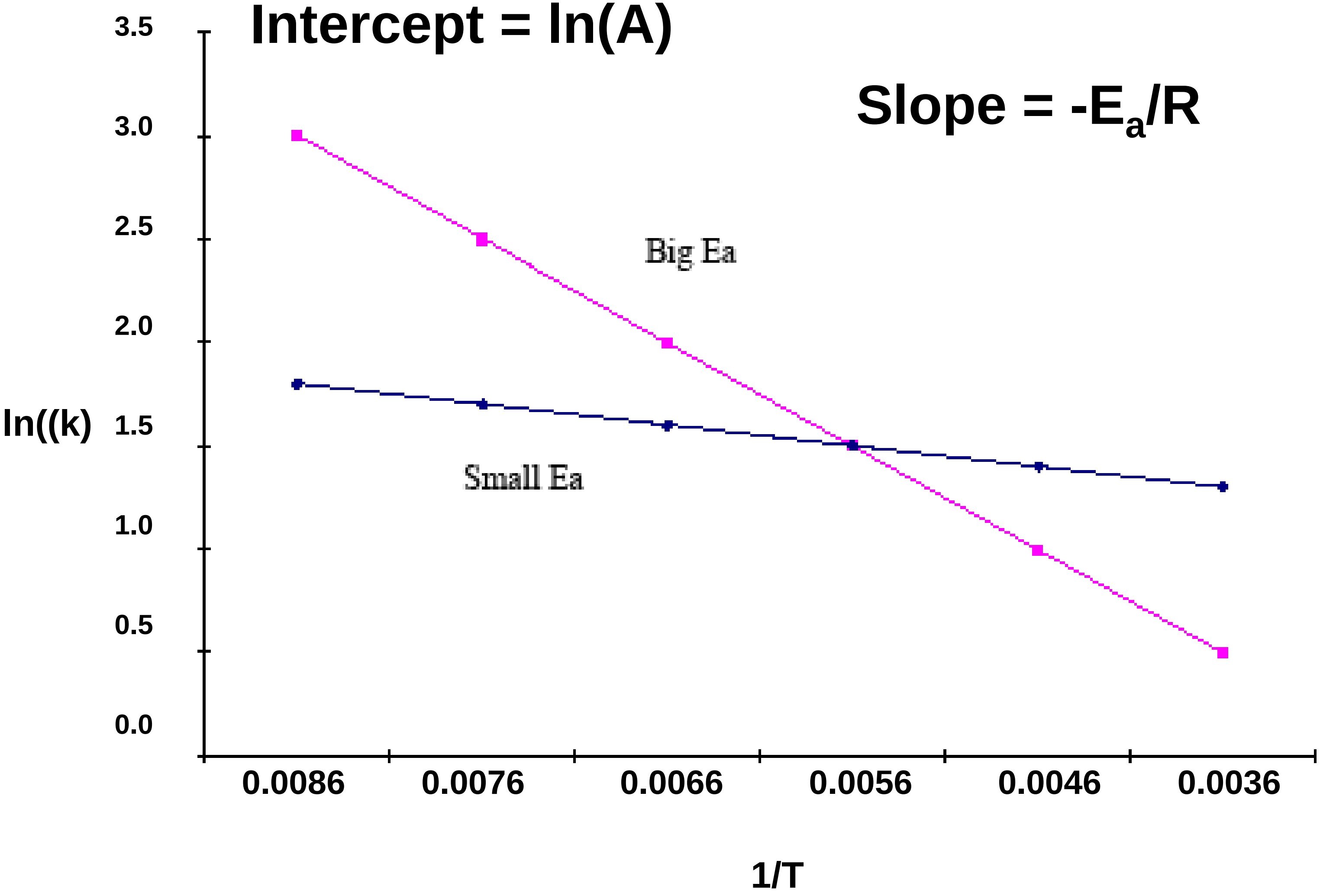
We can plot ln(k) vs. 1/T to determine the activation energy.

$$E_a = -R\frac{d\,ln(k)}{d\left(\frac{1}{T}\right)}$$

A plot of ln k vs. 1/T yields a slope of $-E_a/R$ and an intercept of ln A. You may solve for E_a when you have two rate constants at two temperatures:

$$E_a = -\frac{R\ln\left(\frac{k_2}{k_1}\right)}{\left(\frac{1}{T_2}-\frac{1}{T_1}\right)}$$

Arrhenius plot



Intercept = ln(A)

Slope = $-E_a/R$