2.1: Determination of Activation Parameters

Intuitively, you know that a reaction goes faster as the temperature is raised, as more reactant molecules have the energy needed to overcome the activation barrier to the reaction. The Arrhenius equation relates reaction rate constants (k) and temperature. One of the forms of the Arrhenius equation is:

$$lnk = \frac{-Ea}{RT} + lnA$$

where Ea is the activation energy for the reaction, T is the absolute temperature (in Kelvin) at which a corresponding k is determined, R is the gas constant, and A is a pre-exponential factor. The activation energy may then be extracted from a plot of ln k vs. 1/T, which should be linear. This plot is called an "Arrhenius plot".

Exercise 2.1.1

Recall that y = mx + b.

a. In a so-called “Arrhenius plot” plot, what is the slope?
b. What is the intercept?

Exercise 2.1.2

Using the following data, construct an Arrhenius plot and determine the activation energy (in both kcal/mol and kJ/mol) and the pre-exponential factor.

1/T (K^{-1})	ln k (unitless)
0.00152	3.7
0.00157	3.2
0.00160	2.9
0.00165	2.2
0.00170	1.6

Exercise 2.1.3

Using the following data, construct an Arrhenius plot and determine the activation energy (in both kcal/mol and kJ/mol) and the pre-exponential factor.

T (°C)	k (mol L^{-1} s^{-1})
40	1.3 x 10^{-4}
50	2.2 x 10^{-4}
60	4.0 x 10^{-4}
70	7.5 x 10^{-4}
80	1.4 x 10^{-3}

In practice, activation energies are not often cited in the current literature. Instead, a similar but more useful equation called the Eyring equation is used. The Eyring equation is:

$$ln(\frac{k}{T}) = \frac{-\Delta H^{\ddagger}}{RT} + ln(\frac{k_B}{h}) + \frac{\Delta S^{\ddagger}}{R}$$

where k, T and R are the same as in the Arrhenius equation, k_B is Boltzmann's constant, h is Planck's constant and $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are the enthalpy and entropy of activation, respectively.

Exercise 2.1.4

a. What should be plotted to make an Eyring plot?
b. What is equal to the slope?
c. What is equal to the intercept?

Note that the activation parameters ($\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$) are not the same as the entropy and enthalpy of the reaction, which can usually be calculated from tables of values. Since they depend on how the reaction proceeds, not just the initial and final states of the reaction, they must be determined experimentally. Once that has been done, interpretation of the numerical values provides insight into the mechanism of the reaction.
