CBE 450 Chemical Reactor Fundamentals
Fall, 2009
Homework Assignment #2 Solutions

1. Molecular-Level Description of Reaction Kinetics

(a) What is the transition state of a chemical reaction?
(b) What is the relationship between the energy of the transition state and the activation energy of a reaction?
(c) In the common expression,

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

what are they physical meanings of k_o and $\exp\left(-\frac{E_a}{RT}\right)$?

(d) Where is the entropy difference hidden in this equation?

Solution:

(a) What is the transition state of a chemical reaction?

The transition state of a chemical reaction is a point along the reaction path at which the energy is a maximum.

(b) What is the relationship between the energy of the transition state and the activation energy of a reaction?

The activation energy is the difference between the energy of the transition state and the energy of the reactants.

(c) In the common expression,

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

what are they physical meanings of k_o and $\exp\left(-\frac{E_a}{RT}\right)$?

k_o is the frequency of attempted reactions.

$\exp\left(-\frac{E_a}{RT}\right)$ is the probability of a successful reaction.

(d) Where is the entropy difference hidden in this equation?

The origin of this equation features the exponential of the free energy. The entropy term is simply collected in k_o.

2. Continuum-Level Description of Reaction Kinetics

Fogler P3-4.

3. Experimental Determination of Reaction Kinetics

Consider the bimolecular reaction

$$A + B \rightarrow D$$

The concentration of A is measured as a function of time in an isothermal batch reactor. The reactor is run independently at five different temperatures. Assume the reaction obeys the Arrhenius expression. Use “data set one” located at

http://utkstair.org/clausius/docs/ftp/projdata01.zip

You will only need the first three columns of data set one that provide respectively the temperature of the reactor, the time and the concentration of A. The initial concentration of A for all runs is 2.0 mol/liter. The initial concentration of B for all runs is 2.5 mol/liter.

(a) Write the rate as a function of the concentrations of A and B.
(b) Integrate the rate expression to obtain a relationship between the concentration of A, the temperature and k_o and E_a.
(c) Linearize the equation and generate an Arrhenius plot.
(d) Perform a linear regression and determine k_o and E_a.

Solution:

(a) Write the rate as a function of the concentrations of A and B.

$$r(t) = A^{|\upsilon_A|}B^{|\upsilon_B|}k_o e^{\frac{-E_a}{RT}}$$

(b) Integrate the rate expression to obtain a relationship between the concentration of A, the temperature and k_o and E_a.

$$I_{n,m}(A) - I_{n,m}(A_o) = k_o e^{\frac{-E_a}{RT}}(t - t_o)$$

where

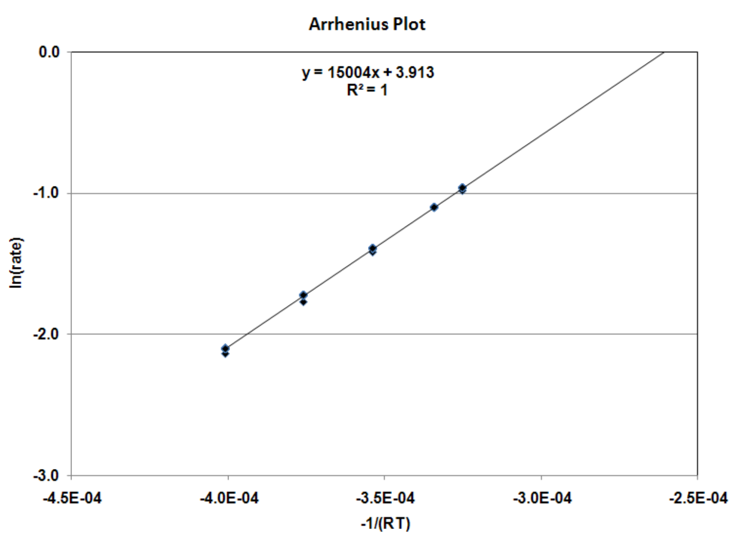
$$\int_{A(t_o)}^{A(t)} \frac{dA}{\upsilon_A A^{|\upsilon_A|}\left\{B(t_o) + \frac{\upsilon_B}{\upsilon_A}[A(t) - A(t_o)]\right\}^{|\upsilon_B|}} = -\frac{1}{n}\int_{x_o}^{x} \frac{dx}{x^n(ax+b)^m} = I_{n,m}(A) - I_{n,m}(A_o)$$

(c) Linearize the equation and generate an Arrhenius plot.

$$\ln\left[\frac{I_{n,m}(A) - I_{n,m}(A_o)}{t - t_o}\right] = \ln[k_o] + \frac{-E_a}{RT} \quad \text{(A.20)}$$

Let $y = \ln\left[\frac{I_{n,m}(A) - I_{n,m}(A_o)}{t - t_o}\right]$, $x = -\frac{1}{RT}$, $m = E_a$, $b = \ln[k_o]$. With these substitutions, we see that our equation is in the form

$$y = mx + b \quad \text{(A.21)}$$



(d) Perform a linear regression and determine k_o and E_a.

activation energy is the slope = 15,004 Joules/mole

ko is the exponential of the intercept = 50.05 liter/mole/sec.