In Class

1. Consider the interconversion of the 'boat' and 'chair' conformations of cyclohexane

$$\text{Boat} \underset{k_r}{\overset{k_f}{\rightleftharpoons}} \text{Chair}$$
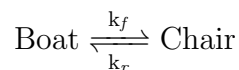
   (a) If the equilibrium constant, K, at 305 K is 1×10^2 and the activation energy, E_a, for the conversion of the chair conformer to the boat conformer (reverse reaction) is 35 kJ mol^{-1} determine the forward and reverse rate constants and the activation energy for the forward reaction at 305 K. Assume that the Arrhenius Equation prefactor, A, is 1×10^{12} s^{-1}.

   (b) Find the forward and reverse rate constants at 298 K. Assume that the Arrhenius Equation prefactor, A, is 1×10^{12} s^{-1}.

   (c) What is the rate law expression for the rate of change of the concentration of the chair conformation?

   (d) If at $t = 0$ the $[\text{Boat}] = [\text{Boat}]_0$ and $[\text{Chair}] = 0$, show that the integrated rate law expression for [Chair] is

$$[C] = \frac{k_f(1 - e^{-(k_f+k_r)t})[B]_0}{k_f + k_r}$$

   (e) What is τ for the return to equilibrium when the temperature is changed from 305 K to 298 K?

   (f) Determine the integrated rate law expression for [Boat]

   (g) Determine the equilibrium concentrations of the Boat and Chair conformations by using their integrated rate law expressions as $t \to \infty$ at 298 K.

   (h) If the temperature is suddenly increased from 298 K to 1000 K, determine the new equilibrium concentrations and the relaxation constant, τ.

Homework

2. You have an equilibrium process where

$$A \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P$$

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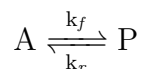
Initially the forward rate constant is equal to $23.7\ \text{s}^{-1}$ and the reverse rate constant is equal to $7.8\ \text{s}^{-1}$. Suddenly, the temperature is changed from 345.2 K to 367.1 K. If the activation energy of the forward process is $24.1\ \text{kJ mol}^{-1}$, and the activation energy of the reverse process is $13.6\ \text{kJ mol}^{-1}$, determine

(a) The equilibrium constant, K, at 367.1 K. ($K = 3.78$)

(b) The time constant, τ for the return to equilibrium. ($\tau = 0.0202$ s)

3. Consider the reaction

$$A + B \underset{k_r}{\overset{k_f}{\rightleftharpoons}} P$$
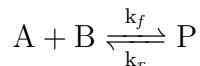
The temperature was suddenly changed on the system at equilibrium. The time constant was measured to be 310 μs, the new equilibrium constant, K, was found to be 0.70, and the new equilibrium concentration of $[P]_{eq} = 0.20$ M.

(a) If $[A]_{eq}=[B]_{eq}$, determine $[A]_{eq}$ and $[B]_{eq}$. ($[A]_{eq} =[B]_{eq} = 0.535$)

(b) Write an expression of $\frac{d[P]}{dt}$ using rate laws. Then define [P], [A], and [B] in terms of the new equilibrium and the advancement of the process towards equilibrium, substitute into your rate law expression and integrate in order to show that

$$\tau = [k_r + k_f([A]_{eq} + [B]_{eq})]^{-1}$$

Hint: Prior to integrating, you will have higher order terms of x. You may assume those are small and disregard them.

(c) Determine k'_f and k'_r for the new temperature. ($k'_r = 1844\ \text{s}^{-1}$ and $k'_f = 1291\ \text{s}^{-1}$).