

Handin Homework 3: Chapter 3 Kinetics

1. Consider the reaction $A + B \rightleftharpoons C$. Assume the initial concentrations are $[A]_o$ and $[B]_o$ with $[C]_o = 0$. Given the extent of the reaction, ξ , the concentration of A during the course the reaction is $[A] = [A]_o - \xi$. The equilibrium extent is ξ_{eq} and the equilibrium concentrations are $[A]_{eq}$, $[B]_{eq}$, and $[C]_{eq}$. The displacement for A is defined as the difference of the current concentration and the equilibrium concentration, $x \equiv [A] - [A]_{eq}$. Prove that:

$$x = \xi_{eq} - \xi \qquad [B] - [B]_{eq} = x \qquad [C] - [C]_{eq} = -x$$

Answer: Given the 1:1 stoichiometry, the current and equilibrium concentrations are:

$$\begin{array}{lll} [A] = [A]_o - \xi & [B] = [B]_o - \xi & [C] = \xi & 1 \\ [A]_{eq} = [A]_o - \xi_{eq} & [B]_{eq} = [B]_o - \xi_{eq} & [C]_{eq} = \xi_{eq} & 2 \end{array}$$

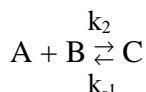
Subtracting Eqs. 2 from Eqs. 1 gives:

$$[A] - [A]_{eq} = \xi_{eq} - \xi \qquad [B] - [B]_{eq} = \xi_{eq} - \xi \qquad [C] - [C]_{eq} = \xi - \xi_{eq} \qquad 3$$

Using the definition of the displacement and the result for A gives: $x = \xi_{eq} - \xi$. Substituting $x = \xi_{eq} - \xi$ into Eqs. 3 gives:

$$[A] - [A]_{eq} = x \qquad [B] - [B]_{eq} = x \qquad [C] - [C]_{eq} = -x \qquad 4$$

2. Consider the integrated rate law for the reaction:



Assume the forward reaction is first order in A and first order in B, and the reverse reaction is first order in C.

(a). Assume the initial concentration of C is zero. Use the results of the first problem to express the rate law in terms of the displacement, x . [Hint: use the equilibrium constant expression.]

(b). Show that the integrated rate law is:

$$\ln \left[\frac{x(x_o + b)}{x_o(x + b)} \right] = - [k_2([A]_{eq} + [B]_{eq}) + k_{-1}] t \qquad \text{with } b = ([A]_{eq} + [B]_{eq} + k_{-1}/k_2)$$

where x_o is the extent at $t = 0$; $x_o = [A]_o - [A]_{eq}$. Integrate the rate law using the standard integral:

$$\int \frac{1}{x^2 + bx} dx = \frac{1}{b} \ln \left(\frac{x}{x + b} \right)$$

Answer: (a). The rate law is: $-\frac{d[A]}{dt} = k_2[A][B] - k_{-1}[C]$ 1

The equilibrium position is given by:

$$K_{eq} = \frac{k_2}{k_{-1}} = \frac{[C]_{eq}}{[A]_{eq}[B]_{eq}} \quad \text{or} \quad k_2[A]_{eq}[B]_{eq} - k_{-1}[C]_{eq} = 0 \quad 2$$

Subtracting Eq. 2 from Eq. 1 gives:

$$-\frac{d[A]}{dt} = k_2[A][B] - k_2[A]_{eq}[B]_{eq} - k_{-1}[C] + k_{-1}[C]_{eq} \quad 3$$

Distributing out the rate constants gives:

$$-\frac{d[A]}{dt} = k_2([A][B] - [A]_{eq}[B]_{eq}) + k_{-1}([C]_{eq} - [C]) \quad 4$$

In terms of the extent:

$$-\frac{dx}{dt} = k_2\{(x + [A]_{eq})(x + [B]_{eq}) - [A]_{eq}[B]_{eq}\} + k_{-1}x \quad 5$$

Using $(x + [A]_{eq})(x + [B]_{eq}) = x^2 + ([A]_{eq} + [B]_{eq})x + [A]_{eq}[B]_{eq}$ simplifies the last equation to give:

$$-\frac{dx}{dt} = k_2[x^2 + ([A]_{eq} + [B]_{eq})x] + k_{-1}x \quad 6$$

Combining the terms in x gives:

$$-\frac{dx}{dt} = k_2x^2 + [k_2([A]_{eq} + [B]_{eq}) + k_{-1}]x \quad 7$$

(b). Separating variables in the last equation gives:

$$\int \frac{1}{x^2 + bx} dx = - \int k_2 dt \quad \text{with } b = ([A]_{eq} + [B]_{eq} + k_{-1}/k_2) \quad 8$$

Using the standard integral gives:

$$\frac{1}{b} \ln\left(\frac{x}{x+b}\right) = -k_2t + c \quad 9$$

Applying the boundary condition at $t = 0$, $x = x_0$ gives the integration constant:

$$c = \frac{1}{b} \ln\left(\frac{x_0}{x_0 + b}\right) \quad 10$$

Substituting Eq. 10 into Eq. 9 gives:

$$\frac{1}{b} \ln\left(\frac{x}{x+b}\right) - \frac{1}{b} \ln\left(\frac{x_0}{x_0 + b}\right) = -k_2t \quad 11$$

Combining the logarithmic terms:

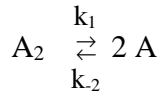
$$\ln\left[\frac{x(x_0 + b)}{x_0(x + b)}\right] = -k_2bt \quad 12$$

Using the definition of b on the right:

$$\ln\left[\frac{x(x_0 + b)}{x_0(x + b)}\right] = - [k_2([A]_{eq} + [B]_{eq}) + k_{-1}] t \quad 13$$

Notice the similarity to the temperature-jump based equations, Eqs. 3.6.8-3.6.10. This result however, is valid over the entire time course of the reaction and not just near equilibrium.

3. Show that the relaxation time for a dissociation:



$$\text{is } \tau = \frac{1}{(k_1 + 4k_{-2}[A]_{eq})}$$

Assume that the reaction is first order in the forward direction and second order in the reverse direction.

Answer: The rate law is given by:

$$v = -\frac{d[A_2]}{dt} = k_1[A_2] - k_{-2}[A]^2 \quad 1$$

Equilibrium is established when the forward and reverse rates are equal:

$$K_{eq} = \frac{k_1}{k_{-2}} = \frac{[A]_{eq}^2}{[A_2]_{eq}} \quad \text{or} \quad k_1[A_2]_{eq} - k_{-2}[A]_{eq}^2 = 0 \quad 2$$

Subtracting Eq. 2 from Eq. 1 references the concentrations to the equilibrium values:

$$-\frac{d[A_2]}{dt} = k_1[A_2] - k_1[A_2]_{eq} - k_{-2}[A]^2 + k_{-2}[A]_{eq}^2 \quad 3$$

Factoring out the rate constants gives:

$$-\frac{d[A_2]}{dt} = k_1([A_2] - [A_2]_{eq}) - k_{-2}([A]^2 - [A]_{eq}^2) \quad 4$$

Eq. 3.1.2 gives the relationship of the concentration changes, $d[A] = -2 d[A_2]$. The displacement in the reactant concentration is $x = [A_2] - [A_2]_{eq}$ and then for the product $[A] - [A]_{eq} = -2x$ or solving for $[A]$:

$$[A] = [A]_{eq} - 2x \quad 5$$

The $[A]^2$ in terms of the displacement is the square of eq. 5:

$$[A]^2 = [A]_{eq}^2 - 4[A]_{eq}x + 4x^2 \approx [A]_{eq}^2 - 4[A]_{eq}x \quad 6$$

However for the last approximation, we assume the displacement is small so that the $4x^2$ is negligible (as we assumed for Eq. 3.6.7). Substituting Eq. 6 into Eq. 4 and using $x = [A_2] - [A_2]_{eq}$, the rate law in terms of the displacements is:

$$-\frac{dx}{dt} = k_1 x + 4k_{-2}[A]_{eq} x \quad 7$$

Distributing out the factor of x gives:

$$\frac{dx}{dt} = -(k_1 + 4k_{-2}[A]_{eq}) x \quad 8$$

Setting the relaxation time to:

$$\tau = \frac{1}{(k_1 + 4k_{-2}[A]_{eq})} \quad 9$$

Substituting this definition for the relaxation time gives: $\frac{dx}{dt} = -\frac{x}{\tau}$ which integrates to:

$$x = x_0 e^{-t/\tau} \quad 10$$

as in Eq. 3.6.11. Once again, neglecting the term in x^2 in Eq. 6 guarantees the relaxation is simple-exponential.