

CYL110 2012-13
Minor 2

Date: Mar. 25, 2013

Time: 1 hour

Useful Information: $R = 8.314 \text{ J/K/mol}$

1. **Imagine following the kinetics of a chemical reaction $0 = \sum_i \nu_i A_i$ by measuring a property Z with a known dependence on the mole numbers, n_i , of the various substances A_i participating in the reaction; that is, we know $Z = Z(n_1, n_2, n_3, \dots, t)$. For a constant volume system, obtain an expression for the rate of the reaction per unit volume, $\frac{1}{V} \frac{d\xi}{dt}$, where ξ is the extent or advancement of the reaction, in terms of the rate of change of Z with time, dZ/dt .**

We are given that

$$Z = Z(n_1, n_2, n_3, \dots, t)$$

Hence

$$\frac{dZ}{dt} = \frac{\partial Z}{\partial n_1} \frac{dn_1}{dt} + \frac{\partial Z}{\partial n_2} \frac{dn_2}{dt} + \frac{\partial Z}{\partial n_3} \frac{dn_3}{dt} + \dots$$

The extent or advancement of the reaction is defined by

$$n_i = n_i^0 + \nu_i \xi$$

where ν_i are the stoichiometric coefficients of the substances A_i . By definition it is positive for products and negative for reactants. For the reaction $\text{H}_2 + 3\text{N}_2 \rightarrow 2\text{NH}_3$, the ν for H_2 , N_2 , and NH_3 are -1 , -3 , and 2 respectively. From the definition of the advancement of the reaction, we get

$$\frac{dn_i}{dt} = \nu_i \frac{d\xi}{dt}$$

Substituting this in the expression for dZ/dt one gets

$$\frac{dZ}{dt} = \frac{\partial Z}{\partial n_1} \nu_1 \frac{d\xi}{dt} + \frac{\partial Z}{\partial n_2} \nu_2 \frac{d\xi}{dt} + \frac{\partial Z}{\partial n_3} \nu_3 \frac{d\xi}{dt} + \dots$$

Thus, the desired expression is

$$\frac{1}{V} \frac{d\xi}{dt} = \frac{1}{V} \frac{\frac{dZ}{dt}}{\nu_1 \frac{\partial Z}{\partial n_1} + \nu_2 \frac{\partial Z}{\partial n_2} + \nu_3 \frac{\partial Z}{\partial n_3} + \dots}$$

2. **The kinetic constants for the hydrolysis of hippurylphenylalanine by the enzyme carboxypeptidase A in 25 mM borate buffer/0.5 M NaCl at pH 9 and 25 °C are $k_2 = k_{\text{cat}} = 61 \text{ s}^{-1}$, $v_{\text{max}} = 10.1 \times 10^{-9} \text{ mol/min}$, and $K_M = 0.29 \times 10^{-3} \text{ M}$. Under identical conditions, the uncatalyzed rate constant for the hydrolysis is $1.3 \times 10^{-10} \text{ s}^{-1}$.**

NOTE THAT THE UNITS OF v_{max} SHOULD HAVE BEEN M/MIN.

- (a) **What is the turnover number of carboxypeptidase A?**

The turnover number is the number of molecules of the substrate turned over to product per second by the enzyme. It is hence equal to k_{cat} , which is 61.

- (b) **What was the initial enzyme concentration for the kinetics studies?**

The maximum rate is $v_{\text{max}} = k_2[E]_0$ from which $[E]_0$ may be determined to be $[E]_0 = 2.81 \times 10^{-12} \text{ M}$.

- (c) **In a plot of $1/v$ vs. $1/[\text{hippurylphenylalanine}]$, what is the slope and intercept?**

For Michaelis-Menten kinetics we know that

$$v = \frac{k_2[E]_0[S]}{K_M + [S]}$$

A plot of $1/v$ vs. $1/[S]$ gives a straight-line with intercept of $1/k_2[E]_0 = 1/v_{\text{max}} = 9.9 \times 10^7 \text{ min/M}$ and slope of $K_M/k_2[E]_0 = K_M/v_{\text{max}} = 2.87 \times 10^4 \text{ min}$.

(d) **What is the half-life of the uncatalyzed reaction?**

For a first-order reaction, which the breakdown of the enzyme-substrate complex is, the half-life is $t_{1/2} = 0.693/k = 5.33 \times 10^9 \text{ s} = 169 \text{ years}$.

(e) **What is the difference in the activation energies of the catalyzed and uncatalyzed reactions?**

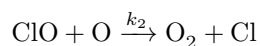
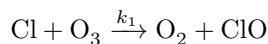
Assuming that the catalyzed and uncatalyzed rate constants show Arrhenius behavior and moreover that their pre-exponential factors are the same, then

$$k_{\text{cat}}/k_{\text{uncat}} = \exp\left(-\frac{\Delta E}{RT}\right),$$

where $\Delta E = E_{a,\text{cat}} - E_{a,\text{uncat}}$.

$$\Delta E = -8.314 \times 298 \times \ln\left(\frac{61}{1.3 \times 10^{-10}}\right) = 8.314 \times 298 \times 26.874 = -66.6 \text{ kJ/mol}$$

3. **Sherwood and Molina showed that the decomposition of ozone ($\text{O} + \text{O}_3 \rightarrow 2 \text{O}_2$) in the upper atmosphere is dramatically changed in the presence of chlorine atoms, which are formed from the photochemical decomposition of chlorofluorocarbons (CFC). The mechanism that they proposed for this decomposition was:**



Confirm that the steady-state rate of the Cl catalyzed ozone decomposition may be written as

$$v_{\text{cat}} = \frac{k_1 k_2 [\text{O}][\text{O}_3] ([\text{Cl}] + [\text{ClO}])}{k_1 [\text{O}_3] + k_2 [\text{O}]}$$

The rate of the reaction, v , is $-\frac{d[\text{O}_3]}{dt} = \frac{1}{2} \frac{d[\text{O}_2]}{dt}$.

$$\frac{d[\text{O}_3]}{dt} = -k_1 [\text{Cl}][\text{O}_3]$$

$$\frac{d[\text{O}_2]}{dt} = k_1 [\text{Cl}][\text{O}_3] + k_2 [\text{ClO}][\text{O}]$$

This implies that v may be written as

$$v = k_1 [\text{Cl}][\text{O}_3] = k_2 [\text{ClO}][\text{O}]$$

In the upper atmosphere there is a steady-state concentration of O, O₃, and Cl. The only reactive intermediate is ClO to which we apply the steady-state approximation.

$$\frac{d[\text{ClO}]}{dt} = k_1 [\text{Cl}][\text{O}_3] - k_2 [\text{ClO}][\text{O}] = 0$$

$$[\text{ClO}] = \frac{k_1 [\text{Cl}][\text{O}_3]}{k_2 [\text{O}]}$$

Here you apply the same trick as in the Michaelis-Menten kinetics where we wrote that $[\text{E}]_0 = [\text{E}] + [\text{ES}]$ - the total amount of Cl in all forms is constant.

$$[\text{Cl}]_0 = [\text{Cl}] + [\text{ClO}]$$

Substituting for [Cl] in terms of [ClO]

$$[\text{Cl}] = \frac{k_2 [\text{O}][\text{ClO}]}{k_1 [\text{O}_3]}$$

in the already obtained expression for ClO yields

$$[\text{ClO}] = \frac{k_1[\text{Cl}]_0[\text{O}_3]}{k_2[\text{O}] + k_1[\text{O}_3]}$$

The rate of the reaction we have shown at the beginning to be

$$v = k_2[\text{ClO}][\text{O}] = k_2[\text{O}] \frac{k_1[\text{O}_3][\text{Cl}]_0}{k_2[\text{O}] + k_1[\text{O}_3]} = \frac{k_1 k_2 [\text{O}][\text{O}_3]}{k_2[\text{O}] + k_1[\text{O}_3]} ([\text{Cl}] + [\text{ClO}])$$

4. Consider the chemical reaction $\text{A} \xrightleftharpoons[k_{-1}]{k_1} 2\text{Z}$. What is the relaxation time in terms of k_1 , k_{-1} , and x_e , where x_e is the concentration of the species Z at equilibrium at the final temperature? Assume starting concentrations of A to be $[\text{A}]_0$ and Z to be zero. Further assume the forward reaction is first order with respect to A and the reverse reaction is second order with respect to Z.

We start by writing the rate of change of the concentration of Z

$$\frac{dZ}{dt} = 2k_1[\text{A}] - 2k_2[\text{Z}]^2$$

Writing the instantaneous concentrations of [A] and [Z] in terms of the deviations ΔA and ΔZ from the equilibrium concentrations $[\text{A}]_{2,\text{eq}}$ and $[\text{Z}]_{2,\text{eq}} = x_{eq}$ respectively, we get

$$\frac{d(x_{eq} + \Delta Z)}{dt} = 2k_1([\text{A}]_{2,\text{eq}} + \Delta A) - 2k_2(x_{eq} + \Delta Z)^2$$

We know that at equilibrium, $\frac{dx_{eq}}{dt} = 0$ and $k_1[\text{A}]_{2,\text{eq}} = k_2 x_{eq}^2$. Moreover, the stoichiometry of the reaction demands that

$$2\Delta A = -\Delta Z$$

Using these results and in addition neglecting the term involving ΔZ^2 we get

$$\frac{d\Delta Z}{dt} = -(k_1 + 4k_2 x_{eq})\Delta Z.$$

This may be rewritten as

$$\frac{d\Delta Z}{\Delta Z} = -(k_1 + 4k_2 x_{eq})dt$$

with the solution

$$\Delta Z(t) = \Delta Z(0) \exp(-(k_1 + 4k_2 x_{eq})t).$$

Comparing this with

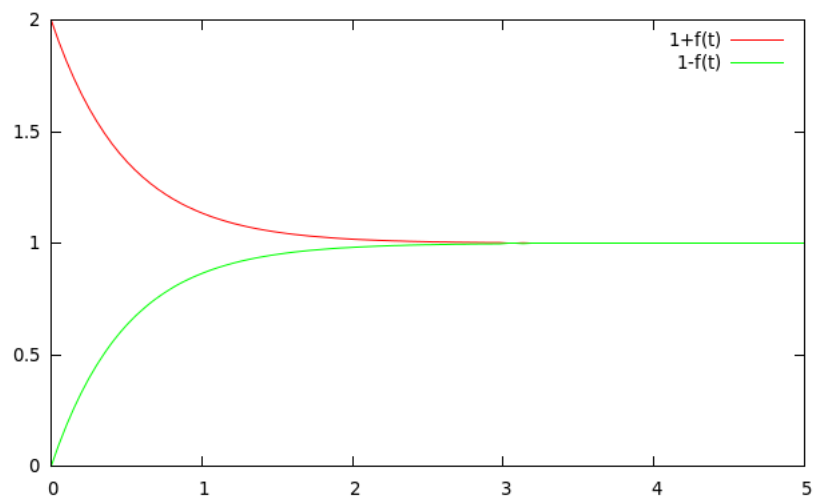
$$\Delta Z(t) = \Delta Z(0) \exp\left(-\frac{t}{\tau}\right).$$

one finds that

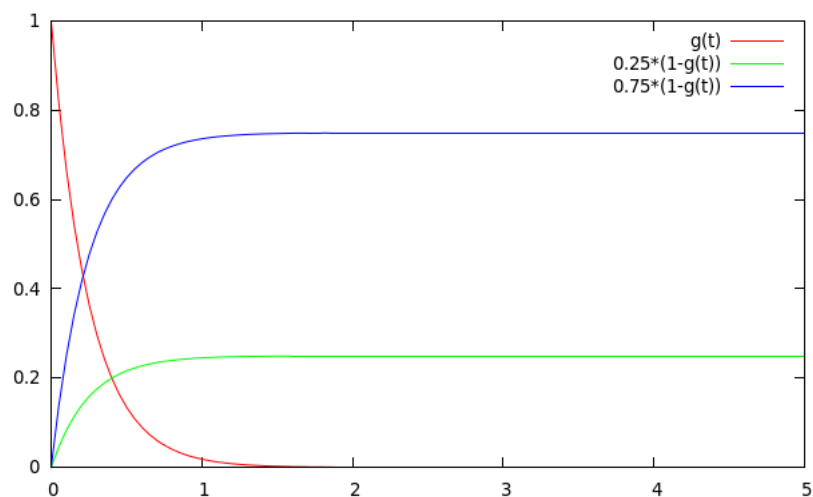
$$\tau = \frac{1}{k_1 + 4k_2 x_{eq}}$$

5. Plot (qualitative sketch showing the relevant features) the fraction present of each species versus the time elapsed for the following cases:

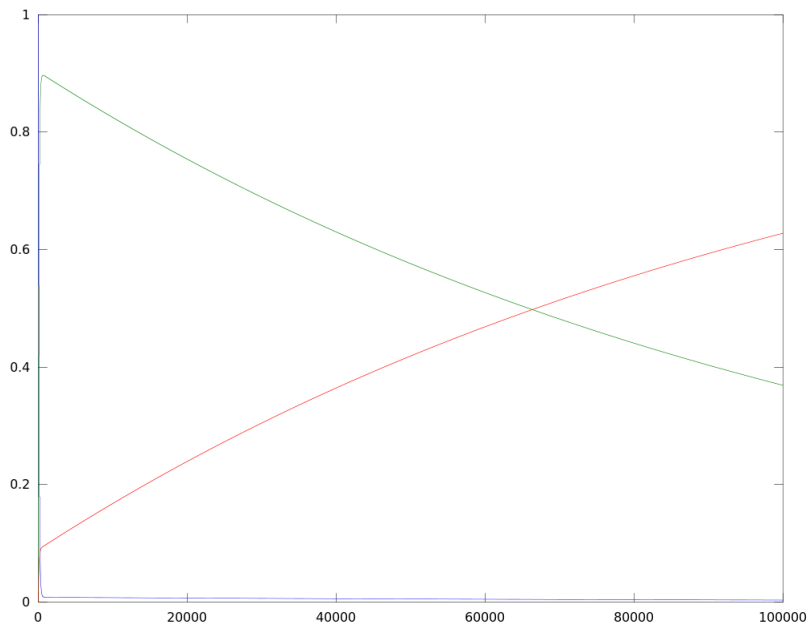
- (a) A in equilibrium with B (first order in both directions, $[\text{A}]_0 \neq 0$ and $[\text{B}]_0 = 0$), with $k_1/k_{-1} = 1$.



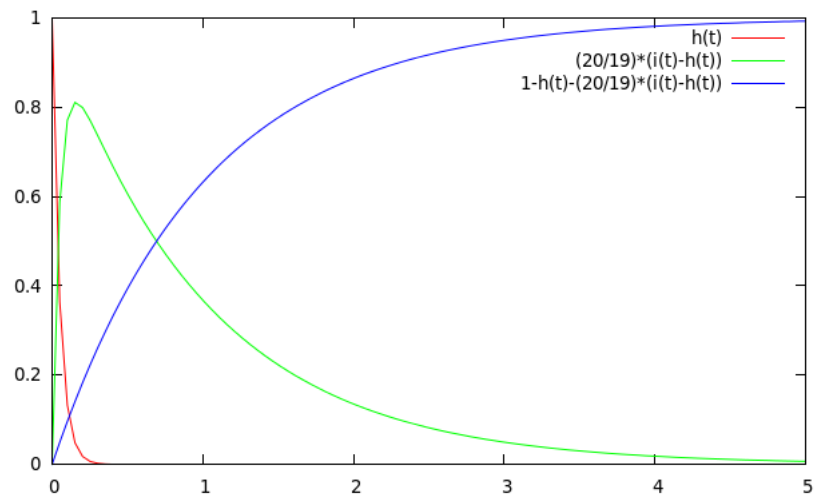
(b) **A** simultaneously decomposing into **B** and **C** with first-order rate constants k_1 and k_2 , respectively, and $k_2/k_1 = 3$ ($[A]_0 \neq 0$, $[B]_0 = 0$, and $[C]_0 = 0$).



(c) **A** in equilibrium with **B** and **C** simultaneously with first-order rate constants (k_1, k_{-1}) and (k_2, k_{-2}) , respectively, and $k_1 = 1 \times 10^{-2}$, $k_{-1} = 1 \times 10^{-4}$, $k_2 = 1 \times 10^{-3}$, and $k_{-2} = 1 \times 10^{-7}$ (with proper units).



(d) A decaying to B and B decaying to C with first-order rate constants of k_1 and k_2 , respectively, and $k_1/k_2 = 20$ ($[A]_0 \neq 0$, $[B]_0 = 0$, and $[C]_0 = 0$).



(e) A decaying to B and B decaying to C with first-order rate constants of k_1 and k_2 , respectively, and $k_2/k_1 = 20$ ($[A]_0 \neq 0$, $[B]_0 = 0$, and $[C]_0 = 0$).

