FCH 361 **Homework #2** **Spring 2020**

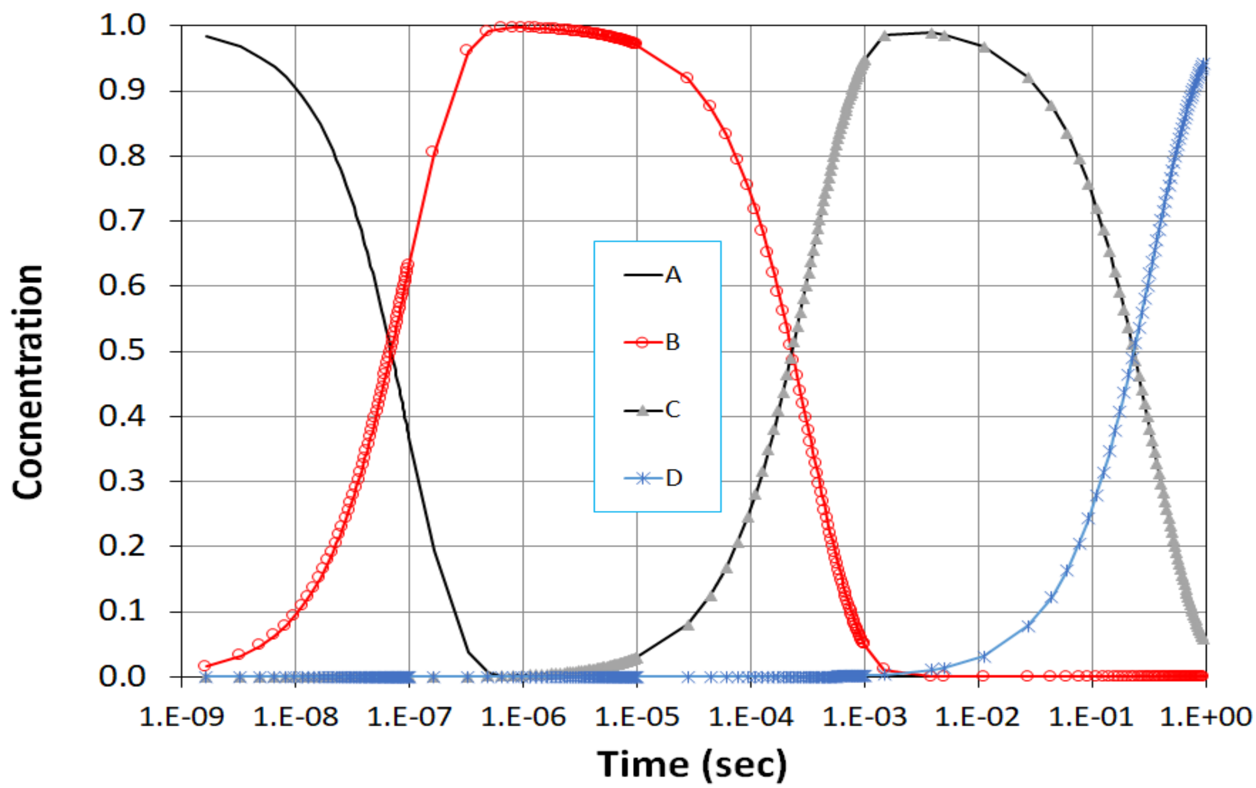
Exercises

A. The graph below shows concentration versus time for the consecutive elementary reactions:

$$A \rightarrow B \rightarrow C \rightarrow D \quad \text{with rate constants} \quad k_a \quad k_b \quad k_c$$

Initial concentrations are $[A]_o$= 1 molar, and $[B]_o = [C]_o = [D]_o = 0$

Estimate the values of k_a, k_b, and k_c from the data in the graph.



B. Given the information below, calculate $[NO_3]_{ss}$:

$N_2O_5 \rightarrow NO_2 + NO_3$	$k_1 = 3.2 \times 10^{-4}\ \text{sec}^{-1}$
$NO_2 + NO_3 \rightarrow N_2O_5$	$k_{-1} = 8.3 \times 10^{-13}\ \text{cm}^3/(\text{molecules sec})$
$NO_3 + NO \rightarrow 2\ NO_2$	$k_2 = 3.3 \times 10^{-11}\ \text{cm}^3/(\text{molecules sec})$
$NO_2 + NO_3 \rightarrow NO + O_2 + NO_2$	$k_3 = 1.4 \times 10^{-16}\ \text{cm}^3/(\text{molecules sec})$

$[NO_2] = [NO] = 1 \times 10^9$ $\quad [N_2O_5] = 1.0 \times 10^{10}$ molecules/cm^3

C. Consider the elementary reaction $X \rightarrow Y \quad k_1$

$E_a = 4.0$ kcal/mole $\quad \Delta H°_r = -5.0$ kcal/mole $\quad \Delta S°_r = -15$ cal/(mole K)

A-factor $= 1.00 \times 10^{-11}$ cm^3/(molecules sec)

For $Y \rightarrow X$ (reaction -1), what is E_a ? The A–factor?

Problems

1) Consider elementary reactions below and constant concentrations of Cl, CH_4, O_2, and NO.

$Cl + CH_4 \rightarrow HCl + \bullet CH_3$ $k_1 = 1.0 \times 10^{-13}$ cm^3/(molecules sec)

$\bullet CH_3 + O_2 \rightarrow CH_3OO\bullet$ $k_2 = 3.5 \times 10^{-12}$ cm^3/(molecules sec)

$CH_3OO\bullet + NO \rightarrow CH_3O\bullet + NO_2$ $k_3 = 8.7 \times 10^{-12}$ cm^3/(molecules sec)

$[CH_4] = 4.4 \times 10^{16}$ $[Cl] = 1.0 \times 10^{4}$ molecules/cm^3

$[O_2] = 5.0 \times 10^{18}$ $[NO] = 1.0 \times 10^{10}$ molecules/cm^3

What are the steady state concentrations of $\bullet CH_3$ and $CH_3OO\bullet$?

Explain whether or not you have sufficient information to compute $[CH_3O\bullet]_{ss}$.

2) GIVEN: the two different expressions given below for the rate constant for the reaction:

$C_4H_9O\bullet + \bullet NO \rightarrow C_4H_9ONO$

$k = 7.8 \times 10^{-12} \exp(+2.85 \text{ kJ/mol}/RT)$ cm^3 $molecule^{-1}$ s^{-1}.

a) In the first expression, what, <u>if anything</u>, is the relationship between 7.8×10^{-12} and the rate constant for collisions?

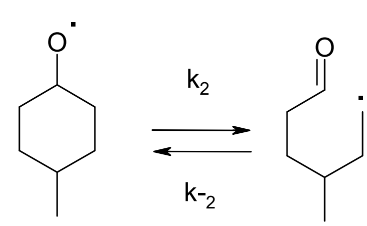
b) In the first expression, what, <u>if anything</u>, is the relationship between and 2.85 kJ/mol and the enthalpy barrier separating reactants and products?

3) Consider the elementary reactions at right and the data:

$k_2 = 1.8 \times 10^{13} \exp(-12.2 \text{ kcal/mole}/RT)$ s^{-1}

$\Delta H°_r = +1.7$ kcal/mole $\Delta S°_r = +11.5$ cal/(mole K).

What is the Arrhenius expression for k_{-2}?



4) Explain why the reaction below could not be an elementary reactions:

A gas phase reaction $A + B \rightarrow$ products follows the rate law $v = k[A][B]$

with $k = 1.4 \times 10^{-11} e^{-1000/T}$ cm^3 $molecule^{-1}$ s^{-1} and $\Delta H°_r = +20$ kJ/mole

5) The graph below shows concentration versus time for the elementary reactions:

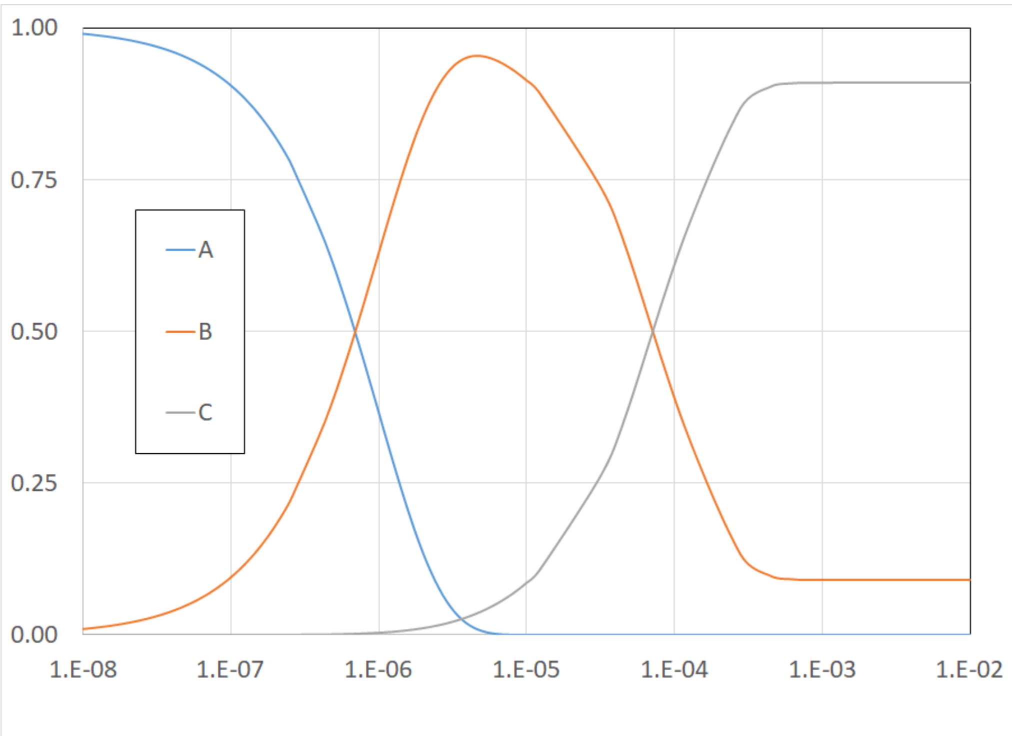
$A \rightarrow B$ k_a

$B \rightarrow C$ k_b

$C \rightarrow B$ k_{-b}

Initial concentrations are $[A]_o$= 1 molar, and $[B]_o$= $[C]_o$ = $[D]_o$ = 0

Estimate the values of k_a, k_b, and k_{-b} from the data in the graph.



6. This question does not count towards your grade. Concentrations of O_2 in the atmosphere are controlled by the following processes. τ, of O_2 in the atmosphere is 4.5×10^3 years

Inputs (kg/year)	
Photosynthesis on land	1.65×10^{14}
Photosynthesis in ocean	1.35×10^{14}

Removal (kg/year)	
Aerobic Respiration	2.3×10^{14}
Microbial Oxidation	5.1×10^{13}
Fuel combustion	1.2×10^{13}
Other	0.7×10^{13}

a) Show from this data that $[O_2]$ in the atmosphere is at (or close to) steady state.
b) Calculate the mass of O_2 in the atmosphere.