so we get

$$[A_i] = k_1 k_2 \dots k_{i-1} [A]_0 \cdot \sum_{j=1}^{i} \alpha_j e^{-k_j t}$$

where α_j can not be determined in a general form.

Note : if $k_1 = k_2 = \dots k_n = k$

$$\mathcal{L}[A_i] = \prod_{j=0}^{i-1} k_j [A]_0 \quad \frac{1}{(p+k)^i}$$

$$[A_i] = k_1 \dots k_{i-1} [A]_0 \quad \frac{[A_i]^{i-1} e^{-kt}}{(i-1)!}$$

$\boxed{2.4}$ Consider the reaction mechanism

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + B$$

$$X \xrightarrow{k_2} C + D$$

(a) Write chemical rate equations for [A] and [X].

(b) Employing the steady-state approximation, show that an effective rate equation for [A] is

$$\frac{d[A]}{dt} = -k_{eff}[A][B].$$

(c) Give an expression for k_{eff} in terms of k_1, k_{-1}, k_2, and [B].

$$A + B \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} X + B$$

$$X \xrightarrow{k_2} C + D$$

(a) $$\frac{d[A]}{dt} = -k_1 [A][B] + k_{-1} [X][B]$$

$$\frac{d[X]}{dt} = +k_1 [A][B] - k_{-1} [X][B] - K_2 [X]$$

(b) let $\frac{d[X]}{dt} = 0$:

$$k_1 [A] [B] = k_{-1} [X] [B] + k_2 [X]$$

$$= \{k_{-1} [B] + k_2\} [X],$$

$$[X]_{ss} = \frac{k_1[A] [B]}{k_{-1} [B] + k_2}$$

$$\frac{d [A]}{dt} = -k_1 [A] [B] + k_{-1} \left\{\frac{k_1[A] [B]}{k_{-1} [B] + k_2}\right\} [B]$$

$$= -k_1 [A] [B] + k_{-1} [A] [B] \left\{\frac{k_1[B]}{k_{-1}[B] + k_2}\right\}$$

$= -k_{eff} [A] [B]$; note [B] is a <u>constant</u>

(c) $$-k_{eff} = + k_{-1} - k_1 \left\{\frac{k_1 [B]}{k_{-1}[B] + k_2}\right\}$$

$$= k_1 \left\{1 - \frac{k_{-1} [B]}{k_{-1}[B] + k_2}\right\}$$

$$= k_1 \left\{1 - \frac{1}{1 + k_2/k_{-1}[B]}\right\}$$

(equivalent expressions, in increasing order of elegance)

$$= k_1 \left\{\frac{\cancel{1} + k_2/k_{-1}[B] - \cancel{1}}{1 + k_2/k_{-1} [B]}\right\}$$

$$= \frac{k_1 k_2/k_{-1} [B]}{1 + k_2/k_{-1} [B]} = \frac{k_1 k_2}{k_{-1} [B] + k_2}$$

2.6 Consider a reaction with two intermediates I_1 and I_2 which both decompose to the same product P by competing parallel steps [S.I. Miller, *J. Chem. Education* 62, 490 (1985)]:

$$A + M \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I_1 \rightarrow P$$
$$I_1 \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} I_2 \rightarrow P$$

(a) Find an expression for dP/dt by applying the steady state approximation with $[I_1]_{ss} = [I_2]_{ss} = 0$.
(b) Find an expression for dP/dt by applying the steady state approximation with $[A]_t = [A]_0 - [I_1] - [I_2] - [P]$.
(c) How do the expressions found in (a) and (b) differ, and what conclusions can be drawn from this difference?

$$A + M \underset{k_1}{\overset{k_{-1}}{\leftrightharpoons}} I_1 \xrightarrow{k_2} P$$
$$I_1 \underset{k_{-3}}{\overset{k_3}{\leftrightharpoons}} I_2 \xrightarrow{k_4} P$$

a. Approximation with $[I_1] = [I_2] \simeq 0$

$$\frac{d[I_1]}{dt} = k_1[A][M] - k_{-1}[I_1] - k_2[I_1] \simeq 0$$

$$\frac{d[I_2]}{dt} = k_3[I_1] - k_3[I_2] - k_4[I_2] \simeq 0$$

$$\frac{d[P]}{dt} = k_2[I_1] + k_4[I_2].$$

$$[I_1] = k_1\frac{[A][M]}{k_2+k_{-1}} \qquad [I_2] = \frac{k_{-3}}{k_3+k_4}[I_1].$$

from the two first steady-state approximation equations on I_1 and I_2

$$\frac{d[P]}{dt} = \frac{k_1 k_2}{k_2+k_{-1}}[A][M] + \frac{k_4 k_3}{k_3+k_4}[I_1].$$

$$\boxed{\frac{d[P]}{dt} = \frac{k_1}{k_2 + k_{-1}}[A][M]\left(k_2 + \frac{k_4 . k_{-3}}{k_3 + k_4}\right)}$$

b. Approximation with $[A] = [A]_0 - [I_1] - [I_2] - [P]$.

$$\frac{d[I_2]}{dt} \simeq 0 \quad \Leftrightarrow \quad [I_2] = \frac{k_{-3}}{k_3 + k_4}[I_1].$$

$$\frac{d[I_1]}{dt} = k_1[A][M] - k_{-1}[I_1] - k_2[I_2].$$

$$= k_1[A]_0[M] - k_1[M][I_1] - k_1[M][I_2]$$
$$- k_1[M][P] - k_{-1}[I_1] - k_2[I_1].$$

$$= k_1[M]([A]_0 - [P]) - (k_1[M] + k_{-1} + k_2)[I_1]$$
$$- k_1[M][I_2]$$

$$= k_1[M]([A]_0 - [P]) - (k_1[M] + k_{-1} + k_2)[I_1]$$
$$- k_1[M]\frac{k_{-3}}{k_3 + k_4}[I_1] \simeq 0$$

$$[I_1] = \frac{k_1[M]([A]_0 - [P])}{k_1[M] + k_{-1} + k_2 + \frac{k_1 k_{-3}}{k_3 + k_4}[M]}$$

$$\frac{d[P]}{dt} = k_2[I_1] + k_4[I_2]$$

$$\boxed{\frac{d[P]}{dt} = \left(k_2 + \frac{k_4 k_{-3}}{k_3 + k_4}\right) \frac{k_1[M]\,([A]_0 - [P])}{k_1[M] + k_{-1} + k_2 + \frac{k_1 k_3}{k_3 + k_4}[M]}}$$

c. If [M] is almost constant, we can integrate the last equation which will provide [P] as a function of time.

$$\frac{d[P]}{\alpha - [P]} = k\,dt. \quad \text{and so on.}$$

If [M] is smaller enough that we can neglect all terms with [M] in the denominator, then we'll get the first expression of $\frac{d[P]}{dt}$!

2.9 The mechanism for the decomposition of ozone into oxygen,

$$2\,O_3 = 3\,O_2$$

is stated to be as follows:

Step 1. $O_3 \rightarrow O_2 + O$, rate constant, k_1

Step 2. $O + O_2 \rightarrow O_3$, rate constant, k_2

Step 3. $O + O_3 \rightarrow 2\,O_2$, rate constant, k_3

The activation energies, in kilojoules per mole, for each of the steps are as follows:

Step 1. $E_{act} = 103$ kJ/mole

Step 2. $E_{act} = 0$

Step 3. $E_{act} = 21$ kJ/mole

(a) Obtain the differential equation for the steady state rate of decomposition of ozone, $-d[O_3]/dt$, in terms of the constants, k_1, k_2 and k_3, the concentration of ozone, $[O_3]$, and the concentration of oxygen, $[O_2]$.

(b) On the basis of the values of E_{act} given above, simplify the expression for $-d[O_3]/dt$ obtained in (a) by eliminating any terms which can become negligible. State clearly the basis for the simplification.

(c) Calculate the energy of activation for the overall reaction.

$$2\,O_3 \longrightarrow 3\,O_2$$

slow $\quad O_3 \xrightarrow{k_1} O_2 + O \qquad E_1 = 103$ kJ/mole

fast $\quad O + O_2 \xrightarrow{k_2} O_3 \qquad E_2 = 0$

fast $\quad O + O_3 \xrightarrow{k_3} 2\,O_2 \qquad E_3 = 21$ kJ/mole

(a) $$-\frac{d[O_3]}{dt} = k_1[O_3] - k_2[O][O_2] + k_3[O][O_3]$$

$$\frac{d[O]}{dt} = k_1[O_3] - k_2[O][O_2] - k_3[O][O_3] = 0 \text{ by steady-state approx.}$$

$$[O]_{ss} = \frac{k_1[O_3]}{k_2[O_2] + k_3[O_3]}$$

$$-\frac{d[O_3]}{dt} = k_1[O_3] - \frac{k_2k_1[O_2][O_3]}{k_2[O_2] + k_3[O_3]} + \frac{k_3k_1[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$= \frac{k_1k_2[O_3][O_2] + k_1k_3[O_3]^2 - k_1k_2[O_2][O_3] + k_3k_1[O_3]^2}{k_2[O_2] + k_3[O_3]}$$

$$\boxed{-\frac{d[O_3]}{dt} = \frac{2\,k_1k_3[O_3]^2}{k_2[O_2] + k_3[O_3]}}$$

(b) It is assumed the O_2, being the stable species, is as or more abundant than O_3 i.e. that

$$[O_2] \geq [O_3]$$

In addition, the energy of activation of the reverse reaction (2) is 0, while that of the forward reaction (3) is 21kJ/mole. Thus (2) has a temperature independent rate, while (3) has standard Arrhenius behavior. Thus at sufficiently low temperature $k_2 >> k_3$ and we may rewrite the rate equation in the form

$$\boxed{-\frac{d[O_3]}{dt} = \frac{2k_1k_3}{k_2}\frac{[O_3]^2}{[O_2]}}$$

(c) The overall rate constant is given by

$$k = \frac{2k_1k_3}{k_2} = \frac{2A_1A_3}{A_2} \; e^{-(E_1 + E_3 - E_2)/k_BT}$$

and the overall activation energy is

$$E_a^T = E_1 + E_3 - E_2 = \underline{124 \text{ kJ/mole}}$$

$\boxed{2.10}$ As a final variation on the theme of Problems 8 and 9, let us consider the reaction between NO and O_3. In this experiment [E. Bar-Ziv, J. Moy, and R. J. Gordon, *J. Chem. Phys.* *68*, 1013 (1978)], it is necessary to distinguish between ozone in its ground (000), excited stretching (001), and excited bending (010) vibrational states.

A CO_2 laser is used to excite ozone from the (000) to the (001) state. The following reactions then ensue in the presence of nitric oxide:

(1) V-V equilibration of ozone:

$$O_3(001) + NO \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} O_3(010) + NO$$

(2-4) reaction of ozone in specified vibrational states with NO to form NO_2:

$$O_3(000) + NO \xrightarrow{k_2} NO_2 + O_2$$
$$O_3(001) + NO \xrightarrow{k_3} NO_2 + O_2$$
$$O_3(010) + NO \xrightarrow{k_4} NO_2 + O_2$$

(5,6) V-T relaxation of ozone:

$$O_3(001) + NO \xrightarrow{k_5} O_3(000) + NO$$
$$O_3(010) + NO \xrightarrow{k_6} O_3(000) + NO$$

The ozone (000) could be followed by its Hartley-band absorption at $\lambda = 254$ nm, and the ozone (001) by its infrared emission at $\lambda = 9\ \mu$m.

(a) Write the kinetic equations, from the above (simplified) mechanism, for the time derivatives of $[O_3(000)]$, $[O_3(010)]$, $[O_3(001)]$, and $[NO_2]$. If the experiment is carried out in a large excess of NO, then pseudo-first-order kinetics may be obtained; rewrite these four expressions in pseudo-first-order, using $K_i = k_i[NO]$.

(b) Find the Laplace transform of the four pseudo-first-order rate equations. (A table of Laplace transforms is included in the Appendix to Chapter 2.) Set up this set of transformed equations in determinantal form.

(c) Find $[O_3(000)]_t$ and $[O_3(010)]_t$ in terms of pseudo-first-order rate coefficients derived from k_1-k_6 and the initial concentrations of $O_3(000)$ and $O_3(001)$ following the laser pulse. Since the experiment is carried out at 300K, and $\nu_2 \approx 700\ \text{cm}^{-1}$ for ozone, the initial concentration of $[O_3(010)]$ cannot be neglected.

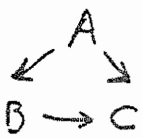
2-15 A somewhat different problem from the fully reversible cyclic mechanism in Problem 2.7 is the following system of reactions*:

$$d[\mathrm{A}]/dt = -k_1[\mathrm{A}] - k_3[\mathrm{A}]$$

$$d[\mathrm{B}]/dt = k_1[\mathrm{A}] - k_2[\mathrm{B}]$$

$$d[\mathrm{C}]/dt = k_2[\mathrm{B}] + k_3[\mathrm{A}]$$

which can be represented as



Using Laplace Transforms and/or a symbolic manipulation program such as MACSYMA or MATHEMATICA, find explicit expressions for $[\mathrm{A}]_t$, $[\mathrm{B}]_t$, and $[\mathrm{C}]_t$ in terms of an initial concentration $[\mathrm{A}]_0 = A_0$. Assume $[\mathrm{B}]_0 = [\mathrm{C}]_0 = 0$.

Equations 3-1, 3-2 and 3-3 are the differential equations that describe the concentrations of *N*-(phenylacetyl)glycyl-D-valine (A), glycyl-D-valine (B) and valine (C), respectively. After normalization, such that A + B + C = 1 at any time, the equation set

$$\frac{d[\mathrm{A}]}{dt} = -k_1[\mathrm{A}] - k_3[\mathrm{A}] \tag{3-1}$$

$$\frac{d[\mathrm{B}]}{dt} = k_1[\mathrm{A}] - k_2[\mathrm{B}] \tag{3-2}$$

$$\frac{d[\mathrm{C}]}{dt} = k_2[\mathrm{B}] + k_3[\mathrm{A}] \tag{3-3}$$

was solved using *Mathematica*[100] to give the following solutions. Equations 3-4, 3-5 and 3-6 descibe the concentration, at a particular time, for *N*-(phenylacetyl)glycyl-D-valine, glycyl-D-valine and valine, respectively. Equation 3-4 was solved for a value of $(k_1 + k_3)$

$$[\mathrm{A}]_t = \left(\frac{1}{e^{(k_1+k_3)t}}\right)\{A\}_0 \tag{3-4}$$

$$[\mathrm{B}]_t = \left(\frac{(-e^{k_2 t} + e^{(k_1+k_3)t})k_1}{e^{(k_1+k_2+k_3)t}(k_1 - k_2 + k_3)}\right)\{A_0\}_0 \tag{3-5}$$

$$[\mathrm{C}]_t = \left(\frac{-(e^{(k_1+k_3)t}k_1) + e^{(k_1+k_2+k_3)t}k_1 + e^{k_2 t}k_2 - e^{(k_1+k_2+k_3)t}k_2 - e^{k_2 t}k_3 + e^{(k_1+k_2+k_3)t}k_3}{e^{(k_1+k_2+k_3)t}(k_1 - k_2 + k_3)}\right)\{A\}_0 \tag{3-6}$$

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I.A. 1. (a), (b) $2\times[N_2O_5 \rightleftarrows NO_2 + NO_3]$

(c) $NO_2 + NO_3 \longrightarrow NO_2 + NO + O_2$

(d) $NO + NO_3 \longrightarrow 2NO_2$

$2N_2O_5 \longrightarrow 4NO_2 + O_2$

$\boxed{c+d}$ is equivalent to $\boxed{f}$, so $\boxed{a+f}$ OK

$\boxed{a,b,c,d}$ or $\boxed{a,c,d}$

2. (a), (b) $N_2O_5 \rightleftarrows NO_2 + NO_3$

(c) $NO + NO_3 \longrightarrow 2NO_2$

$NO + N_2O_5 \longrightarrow 3NO_2$

$\boxed{a,b,d}$

3. (e) $NO_2 + O_3 \longrightarrow NO_3 + O_2$

(b) $NO_2 + NO_3 \longrightarrow N_2O_5$

$2NO_2 + O_3 \longrightarrow N_2O_5 + O_2$

$\boxed{e,b}$

4. (a), (b) $N_2O_5 \rightleftarrows NO_2 + NO_3$

(e) $2\times[NO_2 + O_3 \longrightarrow NO_3 + O_2]$

(F) $2NO_3 \longrightarrow 2NO_2 + O_2$

$2O_3 + N_2O_5 \longrightarrow 3O_2 + N_2O_5$

$\boxed{a,b,e,f}$

2. $R_4 = -\frac{1}{2}\frac{d[O_3]}{dt} = k_4[N_2O_5]^{2/3}[O_3]^{2/3}$ by hypothesis.

$-\frac{d[O_3]}{dt} = k_e[O_3][NO_2]$

$$\left.\begin{aligned}
\frac{d[NO_2]}{dt} &= k_a[N_2O_5] - k_b[NO_2][NO_3] - k_e[NO_2][O_3] + 2k_f[NO_3]^2 = 0 \\
\frac{d[NO_3]}{dt} &= k_a[N_2O_5] - k_b[NO_2][NO_3] + k_e[NO_2][O_3] - 2k_f[NO_3]^2 = 0
\end{aligned}\right\}\ \text{steady-state}$$

The $[N_2O_5]$ concentration is governed by (a) and (b),

$[NO_2]_{ss}[NO_3]_{ss} = \left(\frac{k_a}{k_b}\right)[N_2O_5] = xy, \quad x = \left(\frac{k_a}{k_b}\right)[N_2O_5]/y = c/y$

Thus

$$\begin{aligned}
&\cancel{k_a[N_2O_5]} - \cancel{k_b xy} - k_e x[O_3] + 2k_f y^2 = 0 \\
-\{&\cancel{k_a[N_2O_5]} - \cancel{k_b xy} + k_e x[O_3] - 2k_f y^2 = 0\} \\
\hline
&-2k_e x[O_3] + 4k_f y^2 = 0
\end{aligned}$$

$$k_e(c/y)[O_3] = 2k_f y^2$$

$$k_e c[O_3] = 2k_f y^3$$

$$y = \left(\frac{k_e}{2k_f}\right)^{1/3} c^{1/3}[O_3]^{1/3} = \left(\frac{k_e}{2k_f}\right)^{1/3}\left(\frac{k_a}{k_b}\right)^{1/3}[N_2O_5]^{1/3}[O_3]^{1/3}$$

$$x = [NO_2]_{ss} = \left(\frac{k_a}{k_b}\right)[N_2O_5] \Big/ \left(\frac{k_e}{2k_f}\right)^{1/3}\left(\frac{k_a}{k_b}\right)^{1/3}[N_2O_5]^{1/3}[O_3]^{1/3}$$

$$= \left(\frac{2k_f}{k_e}\right)^{1/3}\left(\frac{k_a}{k_b}\right)^{2/3}[N_2O_5]^{2/3}[O_3]^{-1/3}$$

$$-\frac{d[O_3]}{dt} = k_e[O_3][NO_2]_{ss}$$

$$= k_e\left(\frac{2k_f}{k_e}\right)^{1/3}\left(\frac{k_a}{k_b}\right)^{2/3}[N_2O_5]^{2/3}[O_3]^{2/3} = 2k_4[N_2O_5]^{2/3}[O_3]^{2/3}$$

$$\therefore \boxed{k_4 = 2^{-2/3} k_e^{2/3} k_f^{1/3}\left(\frac{k_a}{k_b}\right)^{1/3}}$$