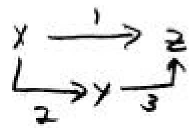
PS1.

1. 

$$x = e^{-k_{12}t}$$

$$y = \frac{k_2}{k_3-k_{12}}\left(e^{-k_{12}t} - e^{-k_3 t}\right)$$

A. $$z = \left[\frac{k_1}{k_{12}} + \frac{k_2 k_3}{k_{12}(k_3-k_{12})}\right]\left(1-e^{-k_{12}t}\right) - \frac{k_2}{k_3-k_{12}}\left(1-e^{-k_3 t}\right)$$

The last eq. comes from

$$\dot{z} = k_1 x + k_3 y = k_1 e^{-k_{12}t} + \frac{k_2 k_3}{k_3-k_{12}}\left(e^{-k_{12}t} - e^{-k_3 t}\right)$$

$$z(t) = k_1 \int_0^\infty e^{-k_{12}t}\,dt + \frac{k_2 k_3}{k_3-k_{12}} \int_0^\infty \left(e^{-k_{12}t} - e^{-k_3 t}\right)dt$$

B. $$z(t=\infty) = \frac{k_1}{k_{12}} + \frac{k_2 k_3}{k_{12}(k_3-k_{12})} - \frac{k_2}{k_3-k_{12}}$$

$$= \frac{1}{k_{12}(k_3-k_{12})}\left[k_1(k_3-k_{12}) + k_2 k_3 - k_2 k_{12}\right]$$

$$= \frac{1}{k_{12}(k_3-k_{12})}\left[k_1 k_3 - k_1 k_{12} + k_2 k_3 - k_2 k_{12}\right]$$

$$= \frac{1}{k_{12}(k_3-k_{12})}\left[k_{12} k_3 - k_{12}^2\right] = 1$$

C. $$z \approx \left[\frac{k_1}{k_{12}} + \frac{k_2 k_3}{k_{12}(k_3-k_{12})}\right] k_{12} t - \frac{k_2 k_3 t}{k_3-k_{12}} = k_1 t$$

$$y = \frac{k_2}{k_3-k_{12}}\left[1 - k_{12}t - 1 + k_3 t\right] = k_2 t$$

Note: $$z(t) = 1 - \left(1 + \frac{k_2}{k_3-k_{12}}\right)e^{-k_{12}t} - \frac{k_2}{k_3-k_{12}}e^{-k_3 t}$$

This is equivalent to the above

D. $k_{12} \simeq k_1$, $e^{-k_{12}t} \simeq 0$

$$y \simeq \frac{-k_2}{k_1}\left(-e^{-k_3 t}\right) = \frac{k_2}{k_1} e^{-k_3 t}$$

$$z \simeq \left[1 - \frac{k_2 k_3}{k_2^2}\right] + \frac{k_2}{k_1} k_3 t \simeq 1$$

E. $k_{12} \simeq k_3$

$$y \simeq \frac{k_2}{-k_2}\left(-e^{-k_3 t}\right) = e^{-k_3 t}$$

$$z \simeq \left(\frac{k_1}{k_2} - \frac{k_2 k_3}{k_2^2}\right) + k_3 t \simeq k_3 t$$

F. $y \simeq \frac{k_2}{k_3} e^{-k_{12} t}$,

$$z \simeq \left(\frac{k_1}{k_{12}} + \frac{k_2 k_3}{k_{12} k_3}\right) k_{12} t - \frac{k_2}{k_3} \simeq k_{12} t$$

3. $\epsilon = 1{,}000$ base e

$= 1{,}000/2.303 = 434.2$ base 10

$\sigma = 1.659 \times 10^{-18}$ base e

$f = \phi \sigma = 0.1$

$\phi = 6.029 \times 10^{16}$ photons/cm^2

$N = \phi A = 1.894 \times 10^{15}$ photons

$\tilde{\nu} = 12{,}500$ cm^{-1} $= 2.483 \times 10^{-19}$ J/photon

$E = 4.70 \times 10^{-4}$ J $= 0.47$ mJ

2. $\dot{A} = -k_1 A + k_2 (A_0 + B_0 - A)$

$= -(k_1 + k_2) A + k_2 (A_0 + B_0)$

$A = C_1 e^{-k_{12} t} + C_2$

$\dot{A} = -C_1 k_{12} e^{-k_{12} t}$

$= -k_{12} \left(C_1 e^{-k_{12} t} + C_2\right) + k_2 (A_0 + B_0)$

$= -k_{12} C_1 e^{-k_{12} t} - k_{12} C_2 + k_2 (A_0 + B_0)$

$k_{12} C_2 = k_2 (A_0 + B_0)$, $\quad C_2 = \frac{k_2}{k_{12}} (A_0 + B_0)$

$A(0) = C_1 + C_2$

$C_1 = A_0 - \frac{k_2}{k_{12}} (A_0 + B_0) = A_0 \frac{k_1}{k_{12}} - B_0 \frac{k_2}{k_{12}}$

$$A = \left[A_0 \frac{k_1}{k_{12}} - B_0 \frac{k_2}{k_{12}}\right] e^{-k_{12} t} + \frac{k_2}{k_{12}} (A_0 + B_0)$$

1.4 The first-order gas reaction $SOCl_2 \longrightarrow SO_2 + Cl_2$ has $k_1 = 2.20 \times 10^{-5}\ s^{-1}$ at 593 K. What percent of a sample of SO_2Cl_2 would be decomposed by heating at 593 K for 1 hour? How long will it take for half the SO_2Cl_2 to decompose?

$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$ first order

$$-\frac{d[SO_2Cl_2]}{dt} = k_1[SO_2Cl_2]$$

$$[SO_2Cl_2]_t = [SO_2Cl_2]_0\ e^{-k_1t}$$

$$t_{1/2} = \frac{\ln 2}{k_1} = \frac{\ln 2}{2.20 \times 10^{-5}\ s^{-1}} = 3.15 \times 10^4\ s$$

$$= 8\ \text{hrs}\ 45\ \text{minutes}$$

at <u>t = 1 hour</u> = 3600 sec

$$\%\ \text{decomposed} = 1 - \frac{[SO_2Cl_2]_t}{[SO_2Cl_2]_o} = 1 - e^{-k_1t} = 1 - .924 = .076,\quad 7.6\%$$

at <u>t = 3 hours</u> = 10800 sec

$$\%\ \text{decomposed} = 1 - e^{-k_1t} = .211,\ \underline{21.1\%}$$

1.8

T-butyl bromide is converted into t-butyl alcohol in a solvent containing 90 percent acetone and 10 percent water. The reaction is given by

$$(CH3)3CBr + H20 \longrightarrow (CH_3)_3COH + HBr$$

The following table gives the data for the concentration of t-butyl bromide versus time [L.C. Bateman, E.D. Hughes, and C.K. Ingold, *J. Chem. Soc.* 960, 1940]:

t(min)	$(CH_3)_3CBr(mol\ l^{-1})$
0	0.1056
9	0.0961
18	0.0856
27	0.0767
40	0.0645
54	0.0536
72	0.0432
105	0.0270

What is the order of the reaction? What is the rate constant of the reaction? What is the half-life of the reaction?

$$(CH_3)CBr + H_2O \longrightarrow (CH_3)_3\ COH + HBr \qquad \text{in } \begin{cases} 90\% \text{ acetone} \\ 10\% \text{ water} \end{cases}$$

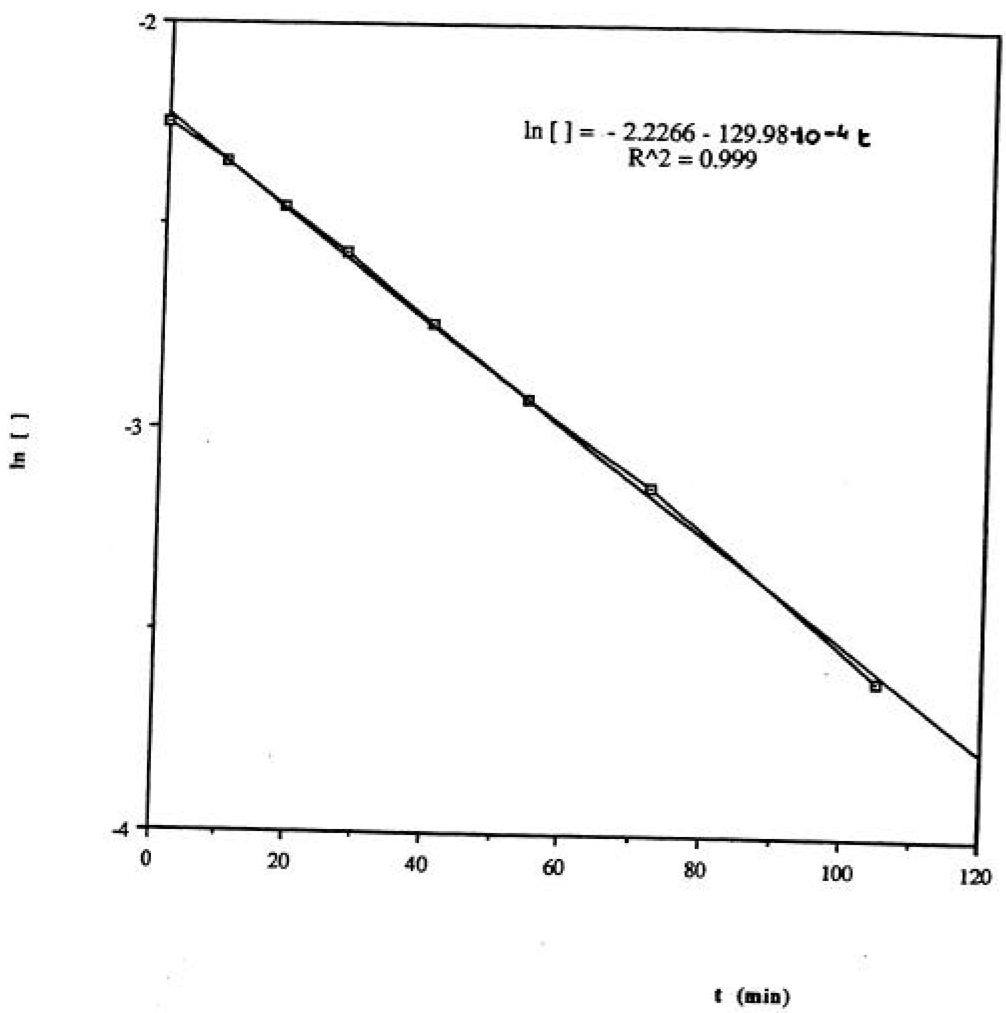
Regarding the tables that give the data for the concentration of t-butyl bromide versus time, as the concentration seems to decrease exponentially, we can think of a first order reaction:

$$\frac{d[(CH_3)_3CBr]}{dt} = -k\,[(CH_3)_3CBr]$$

$$\ln\ [(CH_3)_3CBr = -kt$$

$$[(CH_3)_3CBr] = [(CH_3)_3CBr]_o\, e^{-kt}$$

Let us plot ln $[(CH_3)_3CBr]$ versus time to check this assumption.



t (min)	concentration(mol/l)	ln conc
0.0	0.1056	-2.24810
9.0	0.0961	-2.34237
18.0	0.0856	-2.45807
27.0	0.0767	-2.56785
40.0	0.0645	-2.74109
54.0	0.0536	-2.92621
72.0	0.0432	-3.14191
105.0	0.0270	-3.61192

From these data, we get ln $[(CH_3)_3CBr] = -2.2266 - 1.2998 \times 10^{-2}$ t(min) with a quite good correlation factor, $r^2 = 0.999$.

This is in really good agreement with our assumption:

$$\ln [(CH_3)_3CBr] = \ln [(CH_3)_3CBr]_0 - kt.$$

This is a first-order reaction

$$R = -\frac{d[(CH_3)_3CBr]}{dt} = k[(CH_3)_3CBr].$$

with $k = 0.0130\ min^{-1}$

$= \underline{2.17\ 10^{-4}\ s^{-1}}$

First-order Reaction Half-Life.

$$\ln \frac{[A]}{[A]} = e^{-kt} \qquad [A] = 1/2\ [A].$$

$$t_{1/2} = (\ln 2)/k = \underline{53.3\ min.}$$

This is confirmed by the data:

$t = 0 \quad [(CH_3)_3CBr]_0 = 0.1056$

$t = 54$ min $[(CH_3)_3CBr] = 0.1056$

$\simeq 1/2\ [(CH_3)_3CBr]_0$

1.9

The reaction

$$A + B + C \longrightarrow \text{products}$$

has the rate expression

$$R = -\frac{d[A]}{dt} = k\,[A][B][C]$$

Derive the integral form of the rate expression.

$A + B + C \longrightarrow \text{products}$

$R = -\frac{d[A]}{dt} = k\,[A][B][C]$

define $x = [A]_o - [A]$

then $[A] = [A]_o - x$ and let $[A]_o = A_o$ etc.

$[B] = [B]_o - x$

$[C] = [C]_o - x$

$$\frac{dx}{dx} = k\,(A_o - x)\,(B_o - x)\,(C_o - x)$$

$$\int \frac{dx}{(A_o - x)\,(B_o - x)\,(C_o - x)} = \int_o^t kdt$$

This integral can be performed by separating into partial fractions.

$$\int \left(\frac{L}{A_o - x} + \frac{M}{B_o - x} + \frac{N}{C_o - x}\right) dx = kt$$

$$\frac{L}{A_o - x} + \frac{M}{B_o - x} + \frac{N}{C_o - x} = \frac{1}{(A_o - x)\,(B_o - x)\,(C_o - x)}$$

$L\,(B_o - x)\,(C_o - x) + M\,(A_o - x)\,(C_o - x) + N\,(A_o - x)\,(B_o - x) = 1$

$L\,(B_oC_o - (B_o + C_o)\,x + x^2) + M\,(A_o C_o - (A_o + C_o)\,x + x^2)$

$+ N\,(A_oB_o - (A_o + B_o)\,x + X^2) = 1$

separate by degrees of x:

1:	$L\,(B_oC_o) + M\,(A_oC_o) + N\,(A_oB_o) = 1$	Eq 1
x:	$(B_o + C_o)\,L + (A_o + C_o)\,M + (A_o + B_o)\,N = O$	Eq 2
x^2:	$L + M + N = O$	Eq 3

So we have 3 equations with 3 unknowns. One method to solve for L, M and N is to add and subtract the equations:

$$LB_oC_o + MA_oC_o + NA_oB_o = 1$$

(Eq 2) x B_o gives: $L\,B_o^2 + B_oC_oL + MA_oB_o + MB_oC_o + NA_oB_o + NB_o^2 = 0$

Subtract → $-LB_o^2 + MA_oC_o - MA_oB_o - MB_oC_o - NB_o^2 = 1$

(Eq 3) x B_o^2 gives $\quad LB_o^2 + MB_o^2 + NB_o^2 = 0$

Add $\quad (A_oC_o - A_oB_o - B_oC_o + B_o^2)\,M = 1$

$$(B_o - A_o)(B_o - C_o)\;M = 1$$

$$M = \frac{1}{(B_o - A_o)(B_o - C_o)}$$

Similarly, we can obtain $L = \dfrac{1}{(A_o - B_o)(A_o - C_o)}$

and $N = \dfrac{1}{(C_o - A_o)(C_o - B_o)}$

$$\int_{x_o}^{x} \frac{L}{A_o - x}\,dx + \int_{x_o}^{x} \frac{M}{B_o - x} + \int_{x_o}^{x} \frac{N}{C_o - x}\,dx = kt$$

$$\left(-L\ln\left(\frac{A_o - x}{A_o - x_o}\right) + M\ln\left(\frac{B_o - x}{B_o - x_o}\right) + N\ln\left(\frac{C_o - x}{C_o - x_o}\right)\right)$$

$$= -\left(\frac{1}{(A_o - B_o)(A_o - C_o)}\right)\ln\left(\frac{A_o - x}{A_o}\right) + \frac{1}{(B_o - A_o)(B_o - C_o)}\ln\left(\frac{B_o - x}{B_o}\right)$$

$$+ \frac{1}{(C_o - A_o)(C_o - B_o)}\ln\left(\frac{C_o - x}{C_o}\right)$$

$$= \frac{1}{(A_o - B_o)(B_o - C_o)(A_o - C_o)}\;x$$

$$\left[(B_o - C_o)\;\ln\left(\frac{(A_o - x)}{A_o}\right) - (A_o - C_o)\ln\left(\frac{B_o - x}{B_o}\right) + (A_o - B_o)\ln\left(\frac{C_o - x}{C_o}\right)\right]$$

Let $\quad x = A_o - A_t \quad$ where $\quad A_t = [A]_t$

$$A_o - x = A_t$$

Similarly $\quad B_o - x = B_t, \qquad C_o - x = C_t$

$$\frac{1}{(A_o - B_o)(B_o - C_o)(A_o - C_o)}\left[\ln\left\{\left(\frac{A_t}{A_o}\right)^{B_o - C_o}\left(\frac{B_t}{B_o}\right)^{C_o - A_o}\left(\frac{C_t}{C_o}\right)^{A_o - B_o}\right\}\right] = kt$$