Problem
Set

P35.1) Express the rate of reaction with respect to each species in the following reactions:

a) $2NO(g) + O_2(g) \longrightarrow N_2O_4(g)$

b) $H_2(g) + I_2(g) \longrightarrow 2HI(g)$

c) $ClO(g) + BrO(g) \longrightarrow ClO_2(g) + Br(g)$

a)

$$R = -\frac{1}{2}\frac{d[NO]}{dt} = -\frac{1}{2RT}\frac{dP_{NO}}{dt}$$
$$= -\frac{d[O_2]}{dt} = -\frac{1}{RT}\frac{dP_{O_2}}{dt}$$
$$= \frac{d[N_2O_4]}{dt} = \frac{1}{RT}\frac{dP_{N_2O_4}}{dt}$$

b)

$$R = -\frac{d[H_2]}{dt} = -\frac{1}{RT}\frac{dP_{H_2}}{dt}$$
$$= -\frac{d[I_2]}{dt} = -\frac{1}{RT}\frac{dP_{I_2}}{dt}$$
$$= \frac{1}{2}\frac{d[HI]}{dt} = \frac{1}{2RT}\frac{dP_{HI}}{dt}$$

c)

$$R = -\frac{d[ClO]}{dt} = -\frac{1}{RT}\frac{dP_{ClO}}{dt}$$
$$= -\frac{d[BrO]}{dt} = -\frac{1}{RT}\frac{dP_{BrO}}{dt}$$
$$= \frac{d[ClO_2]}{dt} = \frac{1}{RT}\frac{dP_{ClO_2}}{dt}$$
$$= \frac{d[Br]}{dt} = \frac{1}{RT}\frac{dP_{Br}}{dt}$$

P35.12) A certain reaction is first order, and 540. s after initiation of the reaction, 32.5% of the reactant remains.

a) What is the rate constant for this reaction?

b) At what time after initiation of the reaction will 10% of the reactant remain?

a) The integrated rate law is of the form

$$\ln[R] = \ln[R_0] - kt$$

or

$$\ln\left(\frac{[\mathrm{R}]}{[\mathrm{R}_0]}\right) = -kt$$

Thus at t = 540. s, [A] = 0.325 $[\mathrm{A}]_0$

$$k = -\frac{1}{540\ \mathrm{s}}\ln(0.325)$$
$$k = 0.00208\ \mathrm{s}^{-1}$$
$$k = 2.08\times10^{-3}\ \mathrm{s}^{-1}$$

b) $$t = -\frac{1}{k}\ln\left(\frac{[A]}{[A_0]}\right)$$
$$= -\frac{1}{2.08\times10^{-3}\ \mathrm{s}^{-1}}\ln(0.1)$$
$$t = 1.11\times10^{3}\ s$$

P35.14) You are performing an experiment using ^{3}H (half-life = 4.50×10^3 days) labeled phenylalanine in which the five aromatic hydrogens are labeled. To perform the experiment, the initial activity cannot be lower than 10.0% of the initial activity when the sample was received. How long after receiving the sample can you wait before performing the experiment?

The rate constant can be found from the half-life:

$$k = \frac{\ln 2}{t_{1/2}} = \frac{0.693}{4.5\times10^{3}\ \mathrm{day}}$$
$$k = 1.54\times10^{-4}\ \mathrm{day}^{-1}$$

And so:

$$\ln\left(\frac{[\mathrm{A}]}{[\mathrm{A}]_0}\right) = -kt$$
$$t = -\frac{1}{1.54\times10^{-4}\ \mathrm{day}^{-1}}\left(\ln(0.100)\right)$$
$$t = 1.50\times10^{4}\ \mathrm{days} \approx 41\ \mathrm{years}$$

P35.17) The growth of a bacterial colony can be modeled as a first-order process in which the probability of cell division is linear with respect to time such that $\frac{dN}{N} = \zeta\, dt$, where dN is the number of cells that divide in the time interval dt, and ζ is a constant.

a) Use the preceding expression to show that the number of cells in the colony is given by $N = N_0 e^{\zeta t}$, where N is the number of cell colonies and N_0 is the number of colonies present at $t = 0$.
b) The generation time is the amount of time it takes for the number of cells to double. Using the answer to part (a), derive an expression for the generation time.
c) In milk at 37°C, the bacteria lactobacillus acidophilus has a generation time of about 75 min. Construct a plot of the acidophilus concentration as a function of time for time intervals of 15, 30, 45, 60, 90, 120, and 150 minutes after a colony of size N_0 is introduced to a container of milk.

a) $$\int_{N_0}^{N} \frac{dN}{N} = \xi \int_0^t dt$$

$$\ln(N) - \ln(N_0) = \xi t$$

$$\ln\left(\frac{N}{N_0}\right) = \xi t$$

$$\frac{N}{N_0} = e^{\xi t}$$

b) At the generation time, $N = 2N_0$. Thus, $2N_0 = N_0 e^{\xi t_{gen}}$ or

$$2 = e^{\xi t_{gen}}$$

$$\ln 2 = \xi t_{gen}$$

$$\frac{\ln 2}{\xi} = t_{gen}$$

c) The value of ξ for t_{gen} = 75.0 min can be found.

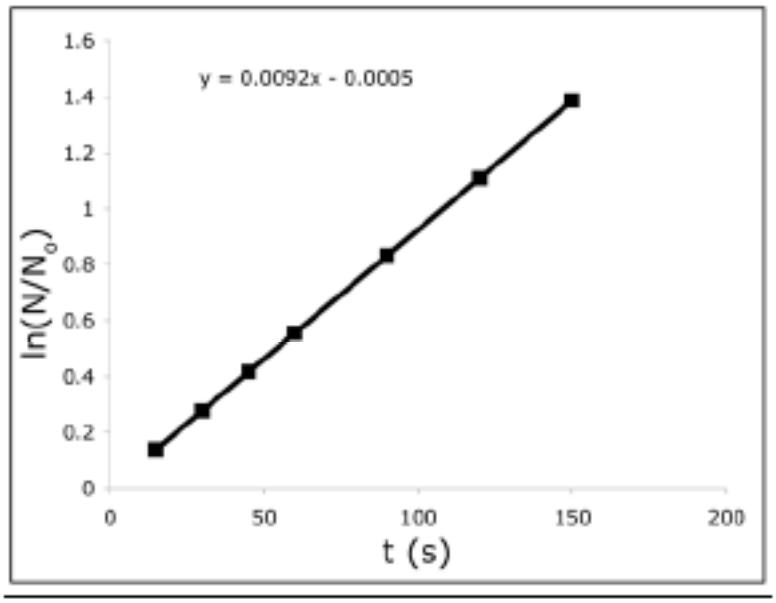
$$\xi = \frac{\ln 2}{75.0 \text{ min}}$$

$$\xi = 0.00924 \text{ min}^{-1}$$

Thus, the following table can be constructed:

t (min)	N/N_0
15	1.148
30	1.319
45	1.515
60	1.741
90	2.297
120	3.031
150	4.000

And the plot of ln (N/N_0) versus time yields



The slope of the line is in agreement with part (b) of this problem.

P35.24) Bacteriorhodopsin (Br) is a protein found in *Halobacterium halobium* that converts light energy into a transmembrane proton gradient that is used for ATP synthesis. After light is absorbed by the protein, the following initial reaction sequence occurs:

$$\mathrm{Br} \xrightarrow{k_1 = 2.0\times10^{12}\ \mathrm{s}^{-1}} \mathrm{J} \xrightarrow{k_2 = 3.3\times10^{11}\ \mathrm{s}^{-1}} \mathrm{K}$$

a) At what time will the maximum concentration of the intermediate *J* occur?
b) Construct plots of the concentration of each species versus time.

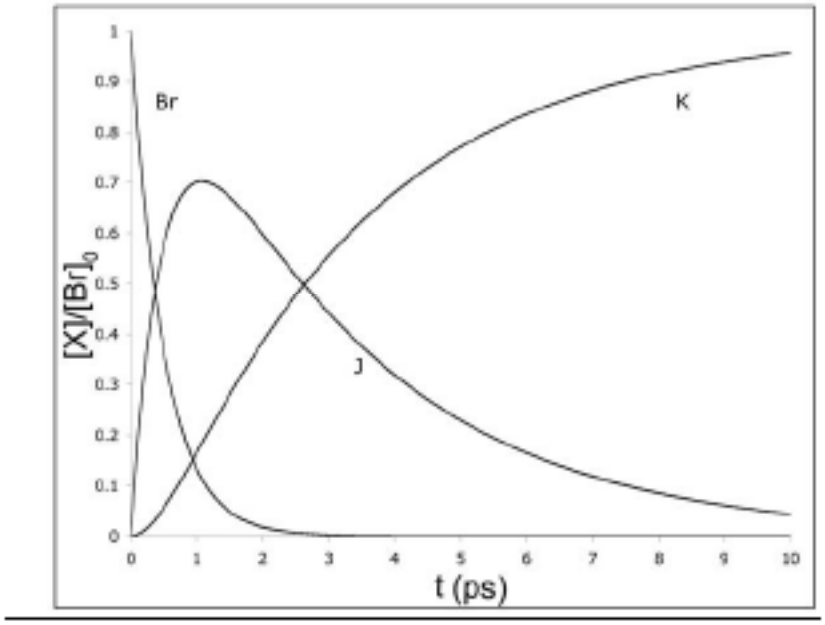
a) $$t_{max} = \frac{1}{k_1 - k_2}\ln\left(\frac{k_1}{k_2}\right)$$

$$= \frac{1}{\left(2.0\times10^{12}\ \mathrm{s}^{-1}\right) - \left(3.3\times10^{11}\ \mathrm{s}^{-1}\right)}\ln\left(\frac{2.0\times10^{12}}{3.3\times10^{11}}\right)$$

$$= \left(5.99\times10^{-13}\ \mathrm{s}^{-1}\right)(1.80)$$

$$= 1.08\times10^{-12}\ \mathrm{s} = 1.08\ \mathrm{ps} \approx 1.1\ \mathrm{ps}$$

b) First, using the expressions for a sequential reaction, the concentration profiles for Br, J, and K were determined using Excel as shown below:



P35.25) Bananas are somewhat radioactive due to the presence of substantial amounts of potassium. Potassium-40 decays by two different paths:

$$^{40}_{19}\mathrm{K} \rightarrow {}^{40}_{20}\mathrm{Ca} + \beta \quad (89.3\%)$$
$$^{40}_{19}\mathrm{K} \rightarrow {}^{40}_{18}\mathrm{Ar} + \beta^{+} \quad (10.7\%)$$

The half-life for potassium decay is 1.3×10^{9} years. Determine the rate constants for the individual channels.

Since this is a branching reaction, we define k_1 as the rate constant for the Ca production, and k_2 as th rate constant for Ar production. Finally, the rate constant for K decay is equal to the sum of k_1 and k_2 that:

$$k = k_1 + k_2 \quad \text{and} \quad \frac{[\mathrm{Ca}]}{[\mathrm{Ar}]} = \frac{k_1}{k_2}$$

Using the definition of the half-life, k is determined as follows:

$$k = \frac{\ln 2}{1.3\times10^{9}\ yr} = 5.33\times10^{-10}\ yr^{-1}$$

Now $k = k_1 + k_2$ where $k_1 = \left(\frac{[\mathrm{Ca}]}{[\mathrm{Ar}]}\right), k_2 = \left(\frac{0.893}{0.107}\right), k_2 = 8.345\ k_2$. Substituting this result into the expression for k yields:

$$k = k_1 + k_2$$
$$5.33\times10^{-10}\ \mathrm{yr}^{-1} = 8.345\ k_2 + k_2$$
$$k_2 = \frac{5.33\times10^{-10}\ \mathrm{yr}^{-1}}{9.345}$$
$$k_2 = 5.70\times10^{-11}\ \mathrm{yr}^{-1}$$
$$k_1 = 4.76\times10^{-10}\ \mathrm{yr}^{-1}$$

P35.30) The rate constant for the reaction of hydrogen with iodine is $2.45 \times 10^{-4}\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 302°C and $0.950\ \mathrm{M}^{-1}\ \mathrm{s}^{-1}$ at 508°C.
a) Calculate the activation energy and Arrhenius preexponential factor for this reaction.
b) What is the value of the rate constant at 400.°C?

a)

$$k(575\ \text{K}) = 2.45\times10^{-4}\ \text{M}^{-1}\text{s}^{-1}$$

$$k(781\ \text{K}) = 0.950\ \text{M}^{-1}\text{s}^{-1}$$

$$2.45\times10^{-4}\ \text{M}^{-1}\ \text{s}^{-1} = Ae^{-E_a/(8.314\ \text{J mol}^{-1}\text{K}^{-1})(575\ \text{K})}$$

$$2.45\times10^{-4}\ \text{M}^{-1}\ \text{s}^{-1} = Ae^{-E_a/4781\ \text{J mol}^{-1}}$$

$$0.950\ \text{M}^{-1}\ \text{s}^{-1} = Ae^{-E_a/(8.314\ \text{J mol}^{-1}\text{K}^{-1})(781\ \text{K})}$$

$$0.950\ \text{M}^{-1}\ \text{s}^{-1} = Ae^{-E_a/6494\ \text{J mol}^{-1}}$$

Taking the ratio of the two rates yields the following for the activation energy:

$$\frac{2.45\times10^{-4}}{0.950} = 2.58\times10^{-4} = \frac{e^{-\frac{E_a}{4781\ \text{J mol}^{-1}}}}{e^{-\frac{E_a}{6494\ \text{J mol}^{-1}}}} = e^{-E_a\left(\frac{1}{4781\ \text{J mol}^{-1}} - \frac{1}{6494\ \text{J mol}^{-1}}\right)}$$

$$\ln\left(2.58\times10^{-4}\right) = -E_a\left(\frac{1}{4781\ \text{J mol}^{-1}} - \frac{1}{6494\ \text{J mol}^{-1}}\right) = -E_a\left(5.52\times10^{-5}\ \text{J}^{-1}\ \text{mol}\right)$$

$$E_a = 1.50\times10^{5}\ \text{J mol}^{-1}$$

Using the activation energy, the pre-exponential factor is determined as follows:

$$A = \left(0.950\ \text{M}^{-1}\text{s}^{-1}\right)e^{1.50\times10^{5}\ \text{J mol}^{-1}/(8.314\ \text{J mol}^{-1}\text{K}^{-1})(781\ \text{K})}$$

$$A = 1.02\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$$

b)

$$k_{673\ \text{K}} = \left(1.02\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}\right)e^{-1.50\times10^{5}\ \text{J mol}^{-1}/(8.314\ \text{J mol}^{-1}\ \text{K}^{-1})(673\ \text{K})}$$

$$= \left(1.02\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}\right)\left(2.30\times10^{-12}\right)$$

$$= 0.0234\ \text{M}^{-1}\ \text{s}^{-1}$$

P35.40) The gas-phase decomposition of ethyl bromide is a first-order reaction, occurring with a rate constant that demonstrates the following dependence on temperature:

Trial Number	Temperature (K)	k (s^{-1})
1	800.	0.036
2	900.	1.410

a) Determine the Arrhenius parameters for this reaction.
b) Using these parameters, determine $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ as described by the Eyring equation.

a) The activation energy is determined by taking the ratio of the rate constants as described by the Arrhenius expression.

$$\frac{k_1}{k_2} = \frac{Ae^{-\frac{E_a}{RT_1}}}{Ae^{-\frac{E_a}{RT_2}}} = e^{-\frac{E_a}{R}\left(\frac{1}{T_1}-\frac{1}{T_2}\right)}$$

$$\frac{0.036}{1.410} = e^{-\frac{E_a}{R}\left(\frac{1}{800.\text{ K}}-\frac{1}{900.\text{ K}}\right)}$$

$$0.0255 = e^{-E_a\left(1.67\times10^{-5}\text{ J}^{-1}\text{ mol}\right)}$$

$$3.67 = E_a\left(1.67\times10^{-5}\text{ J}^{-1}\text{ mol}\right)$$

$$219\text{ kJ mol}^{-1} = E_a$$

Using the activation energy and the rate constant for the first trial, the pre-exponential factor is:

$$0.036\text{ s}^{-1} = Ae^{-\frac{2.19\times10^5\text{ J mol}^{-1}}{\left(8.314\text{ J mol}^{-1}\text{ K}^{-1}\right)(800.\text{ K})}}$$

$$0.036\text{ s}^{-1} = A\left(5.00\times10^{-15}\right)$$

$$7.20\times10^{12}\text{ s}^{-1} = A$$

b) For a unimolecular reaction in solution:

$$A = \frac{ek_BT}{h}e^{\frac{\Delta S^\ddagger}{R}}$$

$$7.20\times10^{12}\text{ s}^{-1} = \frac{(2.718)\left(1.38\times10^{-23}\text{ J K}^{-1}\right)(800.\text{ K})}{\left(6.626\times10^{-34}\text{ J s}\right)}e^{\frac{\Delta S^\ddagger}{R}}$$

$$0.160 = e^{\frac{\Delta S^\ddagger}{R}}$$

$$-1.84 = \frac{\Delta S^\ddagger}{R}$$

$$\Delta S^\ddagger = -15.3\text{ J mol K}^{-1}$$

Furthermore:

$$E_a = \Delta H^\ddagger + RT$$

$$\Delta H^\ddagger = E_a - RT = 219\text{ kJ mol}^{-1} - \left(8.314\text{ J mol}^{-1}\text{ K}^{-1}\right)(800.\text{ K})\left(\frac{1\text{ kJ}}{1000\text{ J}}\right)$$

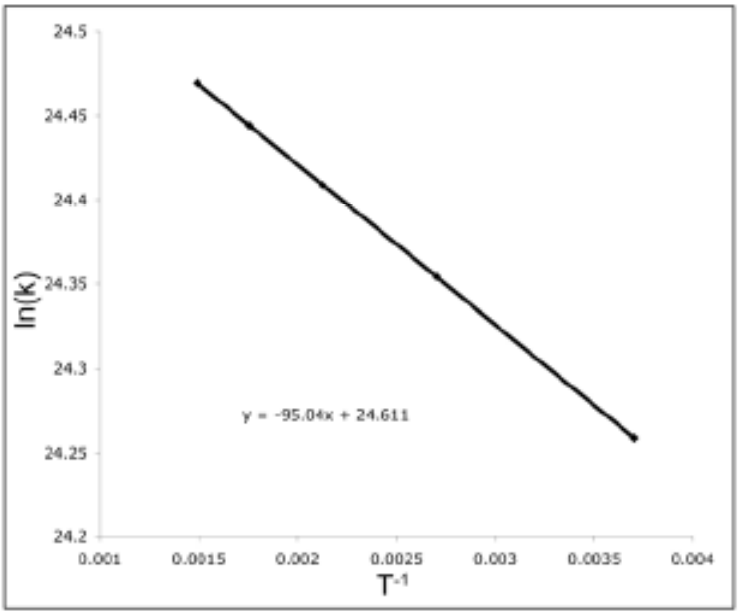
$$= 212.4\text{ kJ mol}^{-1}$$

P35.41) Hydrogen abstraction from hydrocarbons by atomic chlorine is a mechanism for Cl loss in the stratosphere. Consider the reaction of Cl with ethane: $C_2H_6(g) + Cl(g) \longrightarrow C_2H_5(g) + HCl(g)$. This reaction was studied in the laboratory, and the following data was obtained.

T (K)	$10^{-10}\ k$ ($M^{-2}s^{-1}$)
270.	3.43
370.	3.77
470.	3.99
570.	4.13
670.	4.23

a) Determine the Arrhenius parameters for this reaction.
b) At the tropopause (the boundary between the troposphere and stratosphere located approximately 11 km above the surface of the Earth), the temperature is roughly 220 K. What do you expect the rate constant to be at this temperature?
c) Using the Arrhenius parameters obtained in part (a), determine the Eyring parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction.

a) A plot of ln k versus T^{-1} should yield a straight line if the Arrhenius expression is a valid description of the temperature dependence of the rate constant. This plot is given below:



The slope of the line yields the activation energy:

$$-\frac{E_a}{R} = slope$$

$$E_a = -\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)(-95.04\ \text{K})$$

$$= 790\ \text{J mol}^{-1}$$

And the y intercept of the graph yields ln(A):

$$y - \text{int} = \ln(A)$$

$$e^{24.611} = A$$

$$A = 4.88\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$$

b)

$$k = Ae^{-E_a/RT}$$

$$= \left(4.88\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}\right)\exp^{\frac{-790\ \text{J mol}^{-1}}{\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)(220\ \text{K})}}$$

$$= \left(4.88\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}\right)(0.649)$$

$$= 3.17\times10^{10}\ \text{M}^{-1}\ \text{s}^{-1}$$

b) For a second order gas phase reaction:

c)

$$E_a = \Delta H^{\ddagger} + 2RT$$

$$\Delta H^{\ddagger} = E_a - 2RT$$

$$= 790\ \text{J mol}^{-1} - 2\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(220\ \text{K}\right)$$

$$= -2.87\ \text{kJ mol}^{-1}$$

$$A = \frac{e^2 k_B \text{T}}{hc^o} e^{\Delta S^{\ddagger}/R}$$

$$\Delta S^{\ddagger} = R \ln\left(\frac{Ahc^o}{e^2 kT}\right)$$

$$= \left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right) \ln\left(\frac{\left(3.17\times10^{10}\text{M}^{-1}\ \text{s}^{-1}\right)\left(6.626\times10^{-34}\ \text{J s}\right)\left(1\ \text{M}\right)}{e^2\left(1.38\times10^{-23}\ \text{J K}^{-1}\right)\left(220.\ \text{K}\right)}\right)$$

$$= -57.8\ \text{J mol}^{-1}\ \text{K}^{-1}$$

P35.43) Reactions involving hydroxyl radical (OH) are extremely important in atmospheric chemistry. The reaction of hydroxyl radical with molecular hydrogen is as follows:

$$\text{OH}\cdot(g) + \text{H}_2(g) \longrightarrow \text{H}_2\text{O}(g) + \text{H}\cdot(g)$$

Determine the Eyring parameters $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for this reaction where $A = 8 \times 10^{13}\ \text{M}^{-1}\ \text{s}^{-1}$ and $E_a = 42\ \text{kJ mol}^{-1}$.

$$E_a = \Delta H^{\ddagger} + 2RT$$

$$\Delta H^{\ddagger} = E_a - 2RT$$

$$= 4.2\times10^4\ \text{J mol}^{-1} - 2\left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right)\left(300\ \text{K}\right)$$

$$= 3.7\times10^4\ \text{J mol}^{-1} = 37\ \text{kJ mol}^{-1}$$

$$A = \frac{e^2 k_B \text{T}}{hc^o} e^{\Delta S^{\ddagger}/R}$$

$$\Delta S^{\ddagger} = R \ln\left(\frac{Ahc^o}{e^2 kT}\right)$$

$$= \left(8.314\ \text{J mol}^{-1}\ \text{K}^{-1}\right) \ln\left(\frac{\left(8\times10^{13}\text{M}^{-1}\ \text{s}^{-1}\right)\left(6.626\times10^{-34}\ \text{J s}\right)\left(1\ \text{M}\right)}{e^2\left(1.38\times10^{-23}\ \text{J K}^{-1}\right)\left(300.\ \text{K}\right)}\right)$$

$$= 4.57\ \text{J mol}^{-1}\ \text{K}^{-1}$$