

You may work in groups of up to four, as long as every member of the group contributes. The full names of every participating group member should be written clearly on the first page of the problem set. Even if you work in a group, every student needs to upload a problem set as a **single pdf file** on ecampus by 11:59 p.m. on April 23. The file name should be <<lastname_HW9>>. Typically, two problems worth 5 points each will be graded for each problem set total of 10 points.

Since the answers are given, you must show *all work* to earn credit. Write legibly, include units, and box your final answers. If you use a program (Excel, Matlab, Octave) to solve a problem, be sure to include printouts of those graphs, formulas, code, etc., as part of the pdf file. You may convert photos of your work using a phone app (e.g. scanner pro or PDFConverter) or you may use a scanner (e.g. in the library).

These problems are typically more lengthy and difficult (and may require software) than those that will be presented on an exam.

For extra practice on simpler problems, work on the following exercises: 17 A 2a, 5a, 8a, 9a; B 1a, 3a, 4a, 5a, 6a; C 1a, 2a D 1a, 3a, 5a; E 1a, 2a, 3a; F 1a, 2a, 3a, 4a, 5a; G 2a, 3a, 4a; 19 B 4; problem 19 C.1)

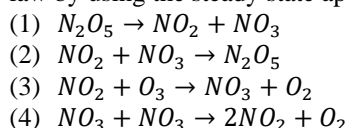
1. Show that the rate of formation of the product (C) in a series of consecutive reactions is $A \rightarrow B \rightarrow C$ is determined by k_1 when $k_1 \ll k_2$ and by k_2 when $k_2 \ll k_1$. This illustrates the concept of rate-limiting step.

Solution 1.
$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 a (\exp(-k_1 t) - \exp(-k_2 t))}{k_2 - k_1}$$

If $k_2 \gg k_1$
$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 a (\exp(-k_1 t) - 1)}{k_2 - k_1}$$
 Rate has exponential dependence on k_1

If $k_1 \gg k_2$
$$\frac{d[C]}{dt} = k_2[B] = \frac{k_1 k_2 a (1 - \exp(-k_2 t))}{k_2 - k_1}$$
 Rate has exponential dependence on k_2

2. The mechanism for the nitrogen-pentoxide catalyzed decomposition of ozone ($2O_3 \rightarrow 3O_2$) is given below. Derive a rate law by using the steady state approximation for NO_2 and NO_3 .



$$v = \frac{1}{2} k_3 [NO_2][O_3] = \left(\frac{k_1^2 k_3 k_4}{4k_2^2} \right)^{\frac{1}{3}} ([N_2O_5][O_3])^{\frac{1}{3}}$$

Solution 2. First, define reaction velocities for each step:

$$v_1 = k_1 [N_2O_5] \quad v_2 = k_2 [NO_2][NO_3] \quad v_3 = k_3 [NO_2][O_3] \quad v_4 = k_4 [NO_3]^2$$

$$v = -\frac{1}{2} \frac{d[O_3]}{dt} = \frac{1}{2} v_3$$

Define the overall reaction in terms of disappearance of reactant:

Use the steady state condition to find relationships among the velocities:

$$\frac{d[NO_2]}{dt} = v_1 - v_2 - v_3 + 2v_4 = 0 \quad \frac{d[NO_3]}{dt} = v_1 - v_2 + v_3 - 2v_4 = 0$$

Comparing the steady-state equations above, $v_3 = 2v_4$ and $v_1 = v_2$

$$v_3 = k_3 [NO_2][O_3] = 2k_4 [NO_3]^2 \quad \text{Solving for } [NO_3] \text{ gives} \quad [NO_3] = \left\{ \frac{k_3 [NO_2][O_3]}{2k_4} \right\}^{\frac{1}{2}}$$

Using the second relationship, $v_1 = k_1[N_2O_5]$ $v_2 = k_2[NO_2][NO_3]$
 Solving for $[NO_2]$ and substituting in for $[NO_3]$ gives

$$[NO_2] = \frac{k_1[N_2O_5]}{k_2[NO_3]} = \frac{k_1[N_2O_5]}{k_2} \cdot \left(\frac{2k_4}{k_3[NO_2][O_3]} \right)^{\frac{1}{2}}$$

$$[NO_2]^{\frac{3}{2}} = \frac{k_1[N_2O_5]}{k_2} \cdot \left(\frac{2k_4}{k_3[O_3]} \right)^{\frac{1}{2}}$$

Bringing all $[NO_2]$ to the same side

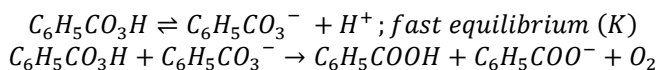
$$[NO_2] = \left(\frac{k_1[N_2O_5]}{k_2} \right)^{\frac{2}{3}} \cdot \left(\frac{2k_4}{k_3[O_3]} \right)^{\frac{1}{3}}$$

Solving for $[NO_2]$ gives

Substituting the expression for $[NO_2]$ into the overall rate expression gives:

$$v = \frac{1}{2} k_3 [NO_2][O_3] = \left(\frac{k_1^2 k_3^2 k_4}{4k_2^2} \right)^{\frac{1}{3}} (N_2O_5 [O_3])^{\frac{2}{3}}$$

3. The decomposition of perbenzoic acid (pba) in water $2C_6H_5CO_3H \rightleftharpoons 2C_6H_5COOH + O_2$ may occur by the following mechanism



Derive an equation showing the dependence of the rate of formation of oxygen on $[H^+]$. (Ans. : $v_2 = k_2 K [BH]^2 / [H^+]$, where $B = C_6H_5COO^-$)

Solution 3. The rate of formation of O_2 is given by $v_2 = k_2 [BH][B^-]$

The equilibrium in the first step is $K = \frac{[B^-][H^+]}{[BH]}$

Using the equilibrium constant to solve for B^- : $[B^-] = K[BH]/[H^+]$

Substituting B^- back into rate law: $v_2 = k_2 K [BH]^2 / [H^+]$

4. The rate constants for the polymerization of vinyl acetate at $60^\circ C$ are $k_p = 2.3 \times 10^3 Lmol^{-1}s^{-1}$ with $E_a = 26 kJ/mole$ and $k_t = 2.9 \times 10^2 Lmol^{-1}s^{-1}$ with $E_a = 13 kJ/mole$. The initiator azobisisobutyronitrile has $k_i = 1.07 \times 10^{-5} s^{-1}$ with $E_a = 130 kJ/mole$. Assume $f=1$ and calculate the rate of polymerization when $[In] = 0.001$, $[M] = 1$ M. Calculate the activation energy for the rate of polymerization. Will the rate and the average chain length increase or decrease with temperature? (Ans **0.014 M; 84.5 kJ/mole; rate increase, kinetic chain length decrease**)

(Noggle 10.61)

$$v_p = k_p \left(\frac{fk_i}{k_t} \right)^{\frac{1}{2}} [M][In]^{\frac{1}{2}} = 2.3 \times 10^3 Lmol^{-1}s^{-1} \left(\frac{1 \cdot 1.07 \times 10^{-5} s^{-1}}{2.9 \times 10^2 Lmol^{-1}s^{-1}} \right)^{\frac{1}{2}} [1 M][0.001 M]^{\frac{1}{2}} = 0.014 M$$

To calculate an effective activation energy, we need an effective rate constant'

$$k_{eff} = k_p \left(\frac{k_i}{k_t} \right)^{\frac{1}{2}}$$

$$E_{a_{eff}} = E_{a_p} + \frac{1}{2} E_{a_i} - \frac{1}{2} E_{a_t} = 26 + \frac{1}{2} (130) - \frac{1}{2} (13) = 84.5 kJ/mole$$

Since the activation energy is positive, the rate will increase with temperature.

To look at the behavior of the kinetic chain length, define an effective rate constant and activation energy from

$$\lambda = k_r [M][In]^{-1/2}, \quad k_r = k_p (4fk_i k_t)^{-1/2}$$

$$k_{eff} = k_p (k_i k_t)^{-1/2}$$

$$E_{a_{eff}} = E_{a_p} - \frac{1}{2} E_{a_i} - \frac{1}{2} E_{a_t} = 26 - \frac{1}{2} (130) - \frac{1}{2} (13) = -45.5 kJ/mole$$

Since the effective activation energy is negative, the kinetic chain length will decrease with an increase in temperature.

5. The kinetics of an enzyme are measured in the presence of an inhibitor. The concentration of this inhibitor is 100 μM .

[S] (μM)	Velocity ($\mu\text{mol}/\text{minute}$)	
	No inhibitor	Inhibitor
3	10.4	2.1
5	14.5	2.9
10	22.5	4.5
30	33.8	6.8
90	40.5	8.1

- (a) What are the values of V_{\max} and K_M in the presence and absence of this inhibitor?
 (b) What type of inhibition is it?

[Ans. (a) No inhibitor: $V_{\max} = 44.6 \mu\text{mol min}^{-1}$. K_M is $1 \times 10^{-5} \text{ M}$, With Inhibitor: $V_{\max} = 8.89 \mu\text{mol min}^{-1}$. K_M is $1 \times 10^{-5} \text{ M}$, the same as without inhibitor.; (b) Noncompetitive]

(<https://www.ncbi.nlm.nih.gov/books/NBK22488/>)

Solutions. A) Make a plot of $1/v_0$ vs. $1/[S]_0$. The intercept is $1/v_{\max}$ and the slope K_M/v_{\max} via the Lineweaver-Burke

$$\text{Equation: } \frac{1}{v_0} = \frac{1}{k_2[E]_0} + \frac{K_M}{k_2[E]_0} \frac{1}{[S]_0}$$

See plot with line fits below.

With Inhibitor

8.888889

9.852444

Without Inhibitor

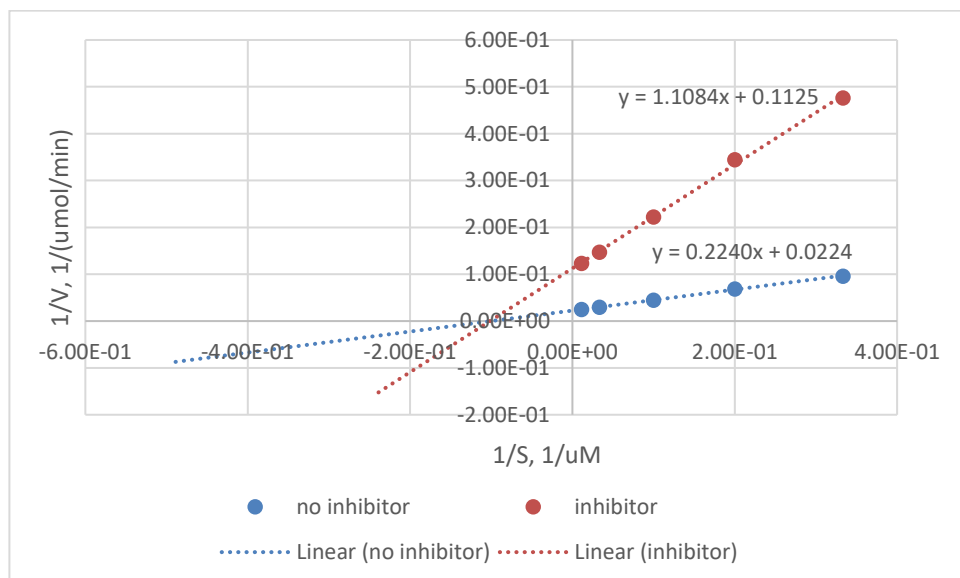
44.64286

10

$V_{\max} = 1/\text{intercept}$

$K_M = \text{slope}/\text{intercept}$

b) Having V_{\max} reduced with K_M unaffected is characteristic of non-competitive inhibition. This can also be recognized in the graph with a common x-intercept for both the inhibited and uninhibited plots. Both the slope and y-intercept are different, however.



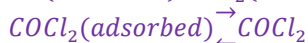
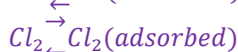
6. For the reaction: $\text{CO} + \text{Cl}_2 = \text{COCl}_2$ the rate expression given below can be obtained:

$$\text{rate} = \frac{k P_{\text{CO}} P_{\text{Cl}_2}}{(1 + \alpha_{\text{CO}} P_{\text{CO}} + \alpha_{\text{COCl}_2} P_{\text{COCl}_2})^2}$$

Show a mechanism consistent with this rate expression. What does the exponent on the denominator imply and what does the lack of an $\alpha_{\text{Cl}_2} P_{\text{Cl}_2}$ term in the denominator suggest?

(<https://authors.library.caltech.edu/25070/6/FundChemReaxEngCh5.pdf>)

Solution. The square term in the denominator indicates that the reaction follows a bimolecular mechanism, where both reactants react at the surface. The lack of a $\alpha_{Cl_2}P_{Cl_2}$ term suggests that the Cl does not adsorb strongly on the surface, however.



The rate determining step will be the reaction at the surface $v = k_3\theta_{CO}\theta_{Cl_2}$ where $\theta_i = \frac{\alpha_i P_i}{1 + \sum_n \alpha_n P_n}$

$$\theta_{CO} = \frac{\alpha_{CO}P_{CO}}{1 + \alpha_{CO}P_{CO} + \alpha_{Cl_2}P_{Cl_2} + \alpha_{COCl_2}P_{COCl_2}}$$

$$\theta_{Cl_2} = \frac{\alpha_2 P_{Cl_2}}{1 + \alpha_1 P_{CO} + \alpha_{Cl_2} P_{Cl_2} + \alpha_{COCl_2} P_{COCl_2}}$$

Substituting in for the coverages gives $rate = \frac{k_3 \alpha_{CO} \alpha_{Cl_2} P_{CO} P_{Cl_2}}{(1 + \alpha_{CO} P_{CO} + \alpha_{Cl_2} P_{Cl_2} + \alpha_{COCl_2} P_{COCl_2})^2}$.

The constants in the numerator can be combined. Also, if $\alpha_{Cl_2} P_{Cl_2}$ is small (adsorption at the surface is weak), the expression simplifies to $rate = \frac{k P_{CO} P_{Cl_2}}{(1 + \alpha_{CO} P_{CO} + \alpha_{COCl_2} P_{COCl_2})^2}$

7. Suppose that a 60-watt lamp, operating with 100% efficiency, emits radiation at a wavelength of 313 nm. How many photons does it emit per second? Suppose that all of the radiation that is emitted is absorbed by heptan-4-one- (di-n-propyl ketone) and that one produce is ethene which is formed with a quantum yield of 0.25. How much ethane is produced in one second? (**Ans. 9.45×10^{19} photons/s; 3.92×10^{-5} moles**)

(Laidler & Meiser) Example 10.7

Solution: The frequency corresponding to 313 nm is the speed of light divided by the wavelength: $\nu = \frac{c}{\lambda} =$

$$\frac{2.998 \times 10^8 \text{ ms}^{-1}}{313 \times 10^{-9} \text{ m}} = 9.578 \times 10^{14} \text{ s}^{-1}$$

The energy of each photon is the frequency multiplied by Planck's constant: $E = h\nu = 6.626 \times 10^{-34} \text{ Js} \cdot$

$$9.578 \times 10^{14} \text{ s}^{-1} = 6.346 \times 10^{-19} \text{ J}$$

The 60-watt lamp emits 60 J each second, and in one second therefore emits: $\frac{60 \text{ J}}{6.346 \times 10^{-19} \text{ J}} = 9.45 \times 10^{19} \text{ photons}$

Since the quantum yield is 0.25, the number of ethene molecules produces in a second is therefore

$$0.25 \frac{\text{product molecules}}{\text{photon}} \cdot 9.45 \times 10^{19} \text{ photons} = 2.36 \times 10^{19} \text{ molecules} = 3.92 \times 10^{-5} \text{ moles}$$

8. The following first order rate constants for the gas phase decomposition of N_2O_5 have been obtained as a function of number density at 298 K.

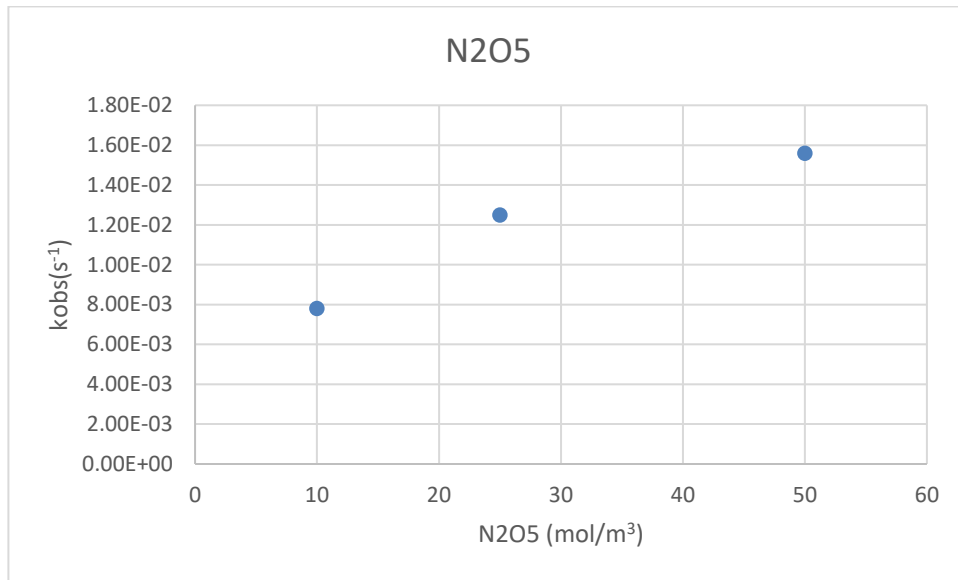
$k_{obs} (s^{-1})$	7.81×10^{-3}	12.5×10^{-3}	15.6×10^{-3}
$[N_2O_5] (mol/m^3)$	10	25	50

Confirm that these data are consistent with the Lindemann mechanism and derive k_1 and $\frac{k_1'}{k_1 k_2}$ for the elementary reactions in the mechanism. What are the units of the two quantities? (**Ans. $\frac{k_1'}{k_1 k_2} = 48.071 \text{ s}$ and $k_1 =$**

$$1.25 \times 10^{-3} \frac{m^3}{mol \text{ s}}$$

(https://chem.libretexts.org/Courses/Remixer_University/Username%3A_marzluff@grinnell.edu/CHM363_Chapter/15%3A_Reaction_mechanisms/15.3%3A_The_Lindemann_Mechanism)

A plot of k_{obs} vs. $[N_2O_5]$ appears to show a leveling off at higher number densities



The decomposition of dinitrogen pentoxide to nitrogen dioxide and nitrogen trioxide



is postulated to take place via two elementary steps

1. $\text{N}_2\text{O}_5 + \text{N}_2\text{O}_5 \rightleftharpoons \text{N}_2\text{O}_5^* + \text{N}_2\text{O}_5$
2. $\text{N}_2\text{O}_5^* \rightarrow \text{NO}_2 + \text{NO}_3$

Using the quasi steady-state approximation solution, then rate equation is:

$$\text{Rate} = k_2[\text{N}_2\text{O}_5]^* = \frac{k_1 k_2 [\text{N}_2\text{O}_5]^2}{k_2 + k_1' [\text{N}_2\text{O}_5]}$$

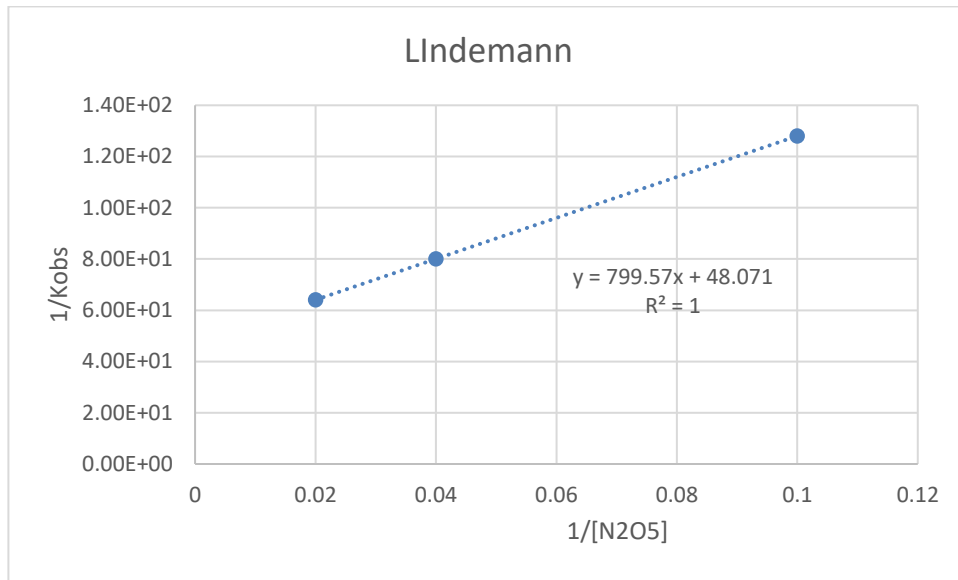
Experiment has shown that the rate is observed as first-order in N_2O_5 sometimes, and second order at other times.

If $k_2 \gg k_1'$, then the rate equation may be simplified by assuming that $k_1' \approx 0$. Then the rate equation is $\text{Rate} = k_1 [\text{N}_2\text{O}_5]^2$, which is *second order*.

If $k_2 \ll k_1'$, then the rate equation may be simplified by assuming $k_2 \approx 0$. Then the rate equation is $\text{Rate} = \frac{k_1 k_2 [\text{N}_2\text{O}_5]^2}{k_1' [\text{N}_2\text{O}_5]} = k_{obs} [\text{N}_2\text{O}_5]$ which is *first order* with $k_{obs} = \frac{k_1 k_2}{k_1'}$

This rate may be rewritten as $\text{Rate} = \frac{k_1 k_2 [\text{N}_2\text{O}_5]}{k_2 + k_1' [\text{N}_2\text{O}_5]} [\text{N}_2\text{O}_5] = k_{obs} [\text{N}_2\text{O}_5]$,

where $\frac{1}{k_{obs}} = \frac{k_1'}{k_1 k_2} + \frac{1}{k_1 [\text{N}_2\text{O}_5]}$. So a plot of $\frac{1}{k_{obs}}$ vs. $\frac{1}{[\text{N}_2\text{O}_5]}$ gives a slope of $\frac{1}{k_1}$ and an intercept of $\frac{k_1'}{k_1 k_2}$



From the plot, the intercept is $\frac{k_1'}{k_1 k_2} = 48.071 \text{ s}$. $k_1 = \frac{1}{\text{slope}} \frac{\text{m}^3}{\text{mol s}} = \frac{1}{799.57} \frac{\text{m}^3}{\text{mol s}} = 1.25 \times 10^{-3} \frac{\text{m}^3}{\text{mol s}}$

9. An amino acid on the surface of an enzyme was labelled covalently with 1,5-I AEDNAS and it is known that the active site contains a tryptophan residue. The fluorescence quantum yield of tryptophan decreased by 15 percent due to quenching by the 1,5-I AEDNAS. What is the distance between the active site and the surface of the enzyme? (**Ans. 2.9 nm**)

The efficiency of resonance energy transfer is defined by $\eta_T = 1 - \phi_F / \phi_{F,0}$ and the distance-dependence of the efficiency is given by $\eta_T = \frac{R_0^6}{R_0^6 + R^6}$, where R is the donor-acceptor distance and R_0 is a characteristic of the particular donor-acceptor pair.

A decline of quantum yield by 15% means that $\phi_F = (1 - 0.15)\phi_{F,0} = 0.85\phi_{F,0}$, so $\eta_T = 1 - 0.85 = 0.15$

$$\begin{aligned} \text{From Table 17G.3, } R_0 &= 2.2 \text{ nm. } \eta_T = 0.15 = \frac{2.2^6}{2.2^6 + R^6} \\ 0.15(2.2^6 + R^6) &= 2.2^6 \\ (0.15 \cdot 2.2^6 + 0.15 \cdot R^6) &= 2.2^6 \\ (0.15 \cdot R^6) &= 2.2^6(1 - 0.15) \\ R^6 &= \frac{0.85 \cdot 2.2^6}{0.15} \\ R &= \left(\frac{0.85 \cdot 2.2^6}{0.15} \right)^{1/6} = 2.9 \text{ nm} \end{aligned}$$