

Unit II General Chemistry II Homework Problems
Part 1, Kinetics

1. (Ex2, Sp15) A kinetic study of the reaction



yielded the data shown on the right.

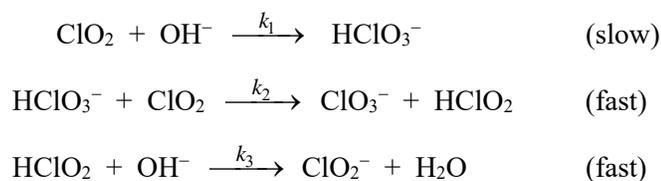
A. What is the rate of appearance of ClO_3^- in experiment 1?
 (Be sure to include units in this and other answers.)

exp	$[\text{ClO}_2] \text{ (M)}$	$[\text{OH}^-] \text{ (M)}$	$-\frac{\Delta[\text{ClO}_2]}{\Delta t} \text{ (M/s)}$
1	0.0500	0.100	0.575×10^{-1}
2	0.100	0.100	2.30×10^{-1}
3	0.100	0.0500	1.15×10^{-1}

B. Determine the experimental rate law.

C. Determine the value of the rate constant based on your answer to Part C.
 (Include units!)

D. The following mechanism was proposed for the above reaction:



- Sketch the potential energy profile for this mechanism.
- Determine the theoretical rate law for this mechanism. Show your work, or explain your reasoning.
- Is this mechanism consistent with the kinetic data? Explain.



2. (Ex2, Su11) A hypothetical kinetic study of the hypothetical reaction



yielded the hypothetical data shown on the right.

A. What would be the value for the rate of appearance of E under the same conditions as experiment 1?

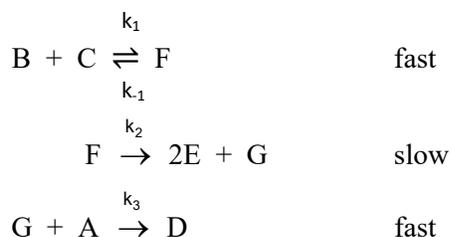
B. Determine the experimental rate law for this reaction.

C. Calculate the rate constant. Be sure to include the correct units.

D. Calculate the rate when $[\text{A}] = 0.21 \text{ M}$, $[\text{B}] = 0.32 \text{ M}$, and $[\text{C}] = 0.26 \text{ M}$.

exp	$[\text{A}] \text{ (M)}$	$[\text{B}] \text{ (M)}$	$[\text{C}] \text{ (M)}$	rate of appearance of D (M/s)
1	0.15	0.15	0.010	1.4×10^{-3}
2	0.15	0.15	0.030	4.2×10^{-3}
3	0.15	0.30	0.030	4.2×10^{-3}
4	0.30	0.15	0.010	2.8×10^{-3}

E. The following mechanism can be proposed for this reaction:

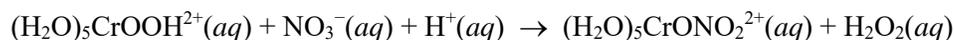


What is(are) the intermediate(s) in this mechanism?

Determine the theoretical rate law for this mechanism.

Does the experimental rate law agree with either of the theoretical rate laws you derived in the previous section?

3. (**Ex2, Sp10**) Transition metal hydroperoxo complexes contain the group MOOH where M is a transition metal ion, and these complexes are believed to be important intermediates in the activation of oxygen in catalytic and biological systems. The reaction below was recently investigated (*Inorg. Chem.* **2010**, *49*, 150–156).



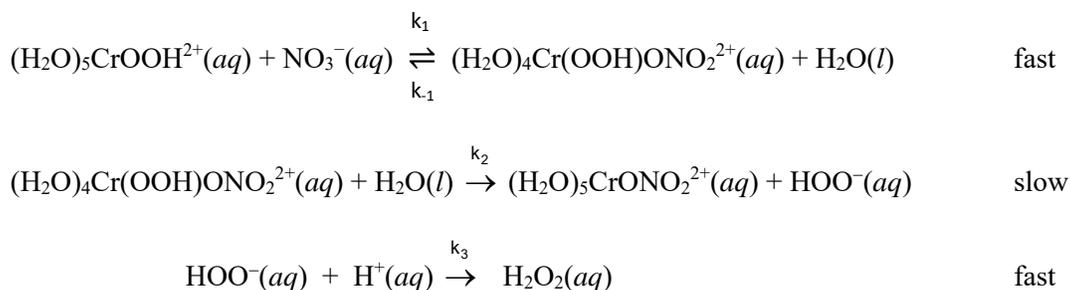
A. Given the following instantaneous rate data at 25°C,

experiment	$[(\text{H}_2\text{O})_5\text{CrOOH}^{2+}]$ (M)	$[\text{NO}_3^-]$ (M)	$[\text{H}^+]$ (M)	rate (M/s)
1	3.0×10^{-4}	0.020	0.010	1.8×10^{-7}
2	3.0×10^{-4}	0.060	0.010	5.4×10^{-7}
3	3.0×10^{-4}	0.020	0.040	7.2×10^{-7}
4	6.0×10^{-4}	0.020	0.010	3.6×10^{-7}

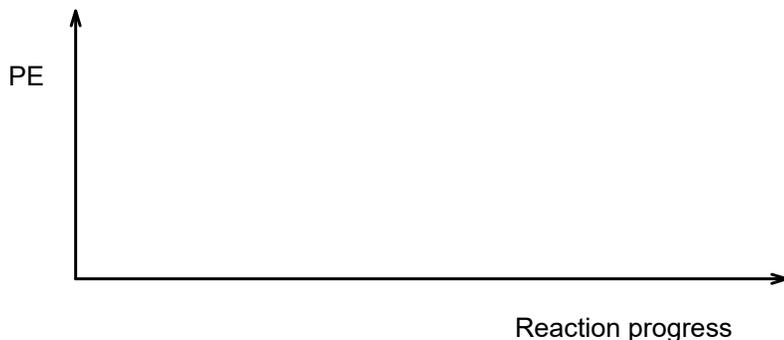
determine the experimental rate law for the above reaction.

- B. What is the rate constant for the above reaction? Be sure to include the correct units.
- C. The rate constant was measured under pseudo-first-order conditions with large excesses of NO_3^- and H^+ . For a particular set of concentrations, a pseudo-first-order rate constant of $2.4 \times 10^{-3} \text{ s}^{-1}$ was obtained. Under these conditions...
- what is the half-life?
 - how long would it take for the concentration of $(\text{H}_2\text{O})_5\text{CrOOH}^{2+}$ to fall from $5.0 \times 10^{-4} \text{ M}$ to $1.5 \times 10^{-4} \text{ M}$?

D. The following mechanism has been proposed for this reaction:



Draw a reaction energy profile diagram consistent with the above diagram.



What is(are) the intermediate(s) in this mechanism?

Determine the theoretical rate law for this mechanism.

4. (**Ex2, Sp16**) We considered the equilibrium between $\text{NO}_2(\text{g})$ and $\text{N}_2\text{O}_4(\text{g})$ in class. The reaction shown below involves two different NO_x compounds.



- A. Use the data in the table to determine the rate law for the reaction.

exp	[NO] (M)	[H ₂] (M)	$-\frac{\Delta[\text{H}_2]}{\Delta t}$ (M/min)
1	0.021	0.065	1.46
2	0.021	0.260	1.46
3	0.042	0.065	5.84

- B. Determine the rate constant. Be sure to include the correct units in your answer.

- C. What is the rate of the reaction when $[\text{NO}] = 0.087 \text{ M}$ and $[\text{H}_2] = 0.18 \text{ M}$?

- D. Suggest two different mechanisms that are consistent with your rate law. Remember that the elementary reactions must add up to give the overall reaction: $2\text{NO}(\text{g}) + \text{H}_2(\text{g}) \rightarrow \text{N}_2\text{O}(\text{g}) + \text{H}_2\text{O}(\text{g})$.

- The first reaction is the rate determining step. (This one should be fairly easy.)
- The first reaction is a rapid equilibrium, and the second reaction is the rate determining step. (This one might seem a little harder, but remember that the intermediate formed in the equilibrium does not have to be a known molecule. It is a reactive intermediate formed along the way.)

5. (**Ex2, Sp12**) Aspirin, $\text{C}_9\text{H}_8\text{O}_4$, slowly decomposes at room temperature by reacting with water in the atmosphere to produce acetic acid, $\text{HC}_2\text{H}_3\text{O}_2$, and 2-hydroxybenzoic acid, $\text{C}_7\text{H}_6\text{O}_3$ (this is why old bottles of aspirin often smell like vinegar):



Concentration and rate data for this reaction are given below.

[C ₉ H ₈ O ₄] (M)	[H ₂ O] (M)	Rate (M/s)
0.0100	0.0200	2.4×10^{-13}
0.0100	0.0800	9.6×10^{-13}
0.0200	0.0200	4.8×10^{-13}

Write the rate law for this reaction and calculate k (be sure to include the correct units).

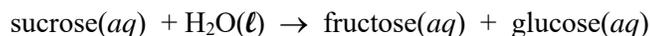
6. (**Ex2, Sp12**) There is a good chance you have never taken an aspirin due to concerns about it causing Reye's Syndrome, especially in children and teens. But I bet you have taken acetaminophen, the active ingredient in Tylenol. Growing concerns about acetaminophen and liver damage, however, have caused pharmacists and physicians to reconsider the rather casual use of this drug. The new recommendation is that adults should limit their intake of acetaminophen to 3 grams per day (the current maximum dose is 4 g/day), and the FDA is considering banning products with over 325 mg per tablet (some prescription products contain 750 mg/tab).

Six grams of acetaminophen can cause liver damage, and 20 grams are considered likely to destroy 70 percent of liver cells and cause death. [An antidote exists, named N-acetylcysteine (N-Ac or “nack”), but it must be administered in a timely manner.]

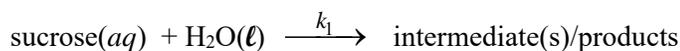
- A. The average rate constant for elimination of acetaminophen is 0.32 hr^{-1} . Assuming an initial dose of 20 g, how long would it take to reduce the amount of acetaminophen in the body to 4g?
- B. What is the half-life for elimination of acetaminophen?

7. (**Ex2, Sp16**) As we transition from chemical kinetics to chemical equilibrium, let's reconsider the problem of trying to sweeten cold tea. Is the sugar less soluble (equilibrium) or slow to dissolve (kinetics)? Recall the observation that sweet tea seems to get sweeter over time.

Sucrose is a disaccharide, composed of the two simple sugars fructose and glucose. Fructose is cheap, sweeter than the other sugars, and it makes us want more.* It seems possible that when sucrose is dissolved in hot tea, it decomposes to form fructose and glucose, which together may be sweeter and more soluble. So let's run the numbers for the reaction



- A. The first-order rate constant for the above reaction is $3.92 \times 10^{-2} \text{ hr}^{-1}$ at 27°C . If the tea is sweetened by adding one cup of sucrose to one gallon of tea, that would correspond to $204 \text{ g}/3785 \text{ mL} = 0.054 \text{ g/mL}$. What would be the concentration of sucrose after 24 hours at 27°C ?
- B. If we use the rule of thumb that the reactant is gone after 10 half-lives, how long would it take for all of the sucrose to decompose?
- C. The rate determining step in the accepted mechanism for the decomposition of sucrose is the initial reaction between sucrose and water:



So why does this reaction follow first-order kinetics? #

#

8. (**Ex2, Su11**) A toxic gas decomposes with a rate constant of $2.7 \times 10^{-2} \text{ hr}^{-1}$ at 25°C .

- A. What is the half-life for this compound at 25°C ?
- B. How long will it take for the amount of gas in the atmosphere to decrease from 19 torr to 0.23 torr (the maximum safe level of exposure)?
- C. Good news – the forecast is for very hot day, with sustained temperatures of 101°F (38.3°C). What is the rate constant for decomposition at that temperature? The activation energy is 22 kJ/mol .

9. (**Ex2, Sp15**) Olanzapine is an orally-administered antipsychotic drug used to treat schizophrenia and bipolar disorder. Like most drugs (95%), olanzapine is eliminated by first-order kinetics. The half-life for olanzapine elimination is 36 hours.

A. Calculate the rate constant for elimination of olanzapine.

(Be sure to include units.)

B. The optimal therapeutic range for olanzapine is 20 to 40 ng/mL. Concentrations of 80 ng/mL are considered to be the upper limit to avoid adverse side effects.

How long would it take for the concentration of olanzapine to drop from 80 ng/mL to 10 ng/mL?

C. By mistake, a patient was given a dose of olanzapine that resulted in a blood serum concentration of 350 ng/mL instead of the desired 35 ng/mL. Calculate* how long will it take for the concentration of olanzapine to drop from 350 ng/mL to 80 ng/mL, the fringe of the “safe zone”?

*Note: Estimating the amount of time based on half-life is not good enough. Calculate the time required.

10. (**Ex2, Su09**) Organizations like UNICEF send millions of dollars’ worth of essential drugs to tropical countries each year. These drugs are often stored under hot and humid conditions for extended periods as they are transported to these countries, so the World Health Organization and UNICEF carried out a joint study to determine the stability of these drugs under such conditions. Most were reasonably stable, but a few showed significant decomposition. For example, the drug ergometrine (also known as ergonovine, it is used to prevent bleeding after child birth) decomposed to 94.2% of the original content after 52 days.

A. Assuming first-order kinetics for the decomposition of ergometrine, calculate the rate constant and half-life for the decomposition of ergometrine under these conditions.

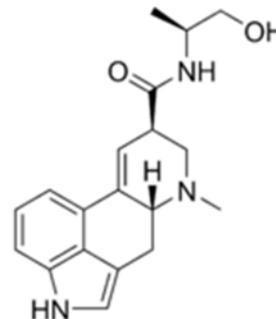
B. Based on the half-life you calculated above, how many days would it take for ergometrine to decompose to 12.5% (one eighth) of its original value? (If you were unable to determine a half-life in part A, then use 167 days as the half-life to answer part B.)

C. It turned out the humidity was a bigger problem than temperature in contributing to the decomposition of these drugs, suggesting that the rate law for decomposition of ergometrine under these conditions might actually be

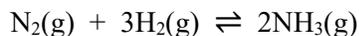
$$\text{rate} = k[\text{ergometrine}][\text{H}_2\text{O}]$$

If the above rate law is correct, explain how the decomposition of ergometrine might appear to follow first-order kinetics as you assumed in part A.

D. The structure of ergometrine is shown on the right. Do you expect this drug to be readily soluble in water, or will it concentrate in the lipid (fatty) tissue? Explain your reasoning.



11. (**Ex2, Sp16**) We briefly considered the Haber process as our “graduation exercise,” but not the mechanism.



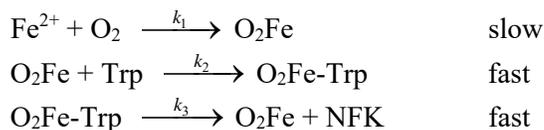
At the surface of the catalyst, N_2 and H_2 are separated into atoms, and the atoms combine to form NH_3 . Dissociation of N_2 is generally accepted as the rate-determining step, followed by formation of NH . The activation energy for forming NH is 116.8 kJ/mol without a catalyst and 97.4 kJ/mol with a ruthenium cluster catalyst. The rate constant at 320 K is $1.75 \times 10^{-4} \text{ s}^{-1}$ without the catalyst. (*J. Phys. Chem. Lett.* **2013**, 4, 3779–3786)

A. What is the rate constant at 320 K with the catalyst?

B. Speculate on why dissociation of N_2 is the rate determining step instead of dissociation of H_2 .

12. (Ex2, Sp'12) Indoleamine 2,3-dioxygenase catalyzes the oxidation of L-tryptophan (Trp) to *N*-formylkynurenine (NFK); see *J. Am. Chem. Soc.* **2012**, *134*, 3034-3041. (Yes, the same L-tryptophan that supposedly makes you sleepy after a turkey dinner. Turns out that's a myth.)

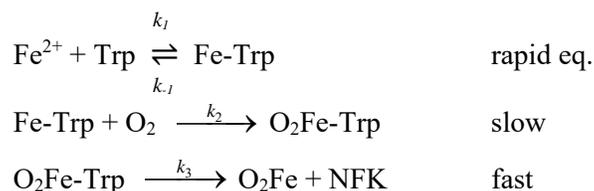
A. The simplified mechanism at low concentrations of L-tryptophan is given below.



What is the theoretical rate law for this mechanism?

Be sure to include the individual k values in your rate law.

B. At high concentrations of L-tryptophan, the mechanism changes.

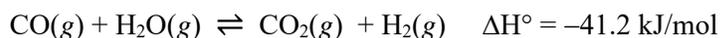


What is the theoretical rate law for this mechanism?

Be sure to include the individual k values in your rate law.

C. If you knew the experimental rate law, could you use it to distinguish between the two mechanisms?

13. (Ex2, Sp'14) We worked a fairly extensive equilibrium problem in class based on the water gas shift (WGS) reaction, but we never discussed the kinetics of this very important process, so let's do that now. Recall that the chemical equation for the WGS reaction is



The kinetics of the WGS reaction has been studied extensively, and it is quite complicated, but if you focus on the initial rate of the reaction and work under conditions of excess $\text{H}_2\text{O}(g)$, then the reaction follows first-order kinetics (J. Picou, et al. 2008 Conference of the American Institute of Chemical Engineers) with respect to the concentration of CO. So under these conditions, the experimental rate law for the uncatalyzed reaction is

$$-\frac{\Delta[\text{CO}]}{\Delta t} = k[\text{CO}] \quad \text{where} \quad k = 7.0 \times 10^{-14} \text{ s}^{-1} \text{ at } 100^\circ\text{C}.$$

- A. Assume that you start with an initial CO pressure of 0.100 atm. How long will it take for the pressure of CO to decrease to 0.010 atm?
- B. The kinetic study described above yielded an activation energy of 132.5 kJ/mol for the reaction. In the industrial world, this reaction is always carried out with a catalyst. Assuming that the catalyst can lower the activation energy by a factor of two, what would be the rate constant with the catalyst, keeping all other conditions the same?
- C. Or you could determine the rate law by measuring the initial rate for specific concentrations or pressures of $\text{CO}(g)$ and $\text{H}_2\text{O}(g)$. Suppose you carried out another kinetic study using a new catalyst. Keeping the pressure of $\text{CO}(g)$ at 0.100 atm, you increased the pressure of $\text{H}_2\text{O}(g)$ from 0.100 atm to 0.300 atm, and the rate of the reaction ($-\Delta[\text{CO}]/\Delta t$) increased from 5.0×10^{-6} atm/s to 4.5×10^{-5} atm/s. What is the rate law (assuming the reaction is still first-order in CO) and rate constant (be sure to include the units) with the new catalyst?

14. (**Ex3, Sp14**) In Exam Two we considered the kinetics of the water gas shift (WGS) reaction



A kinetic study reported at the 2008 Conference of the American Institute of Chemical Engineers. Working under the conditions of excess $\text{H}_2\text{O}(g)$, the reaction follows first-order kinetics with respect to the concentration of CO. So under these conditions, the experimental rate law for the uncatalyzed reaction is

$$-\frac{\Delta[\text{CO}]}{\Delta t} = k[\text{CO}] \quad \text{where} \quad k = 7.0 \times 10^{-14} \text{ s}^{-1} \text{ at } 100^\circ\text{C}.$$

The activation energy under these conditions was determined to be 132.5 kJ/mol. In Part B of Question III we considered how the rate constant would change if a catalyst was found that lower the activation energy by a factor of two, keeping all other conditions the same. The result was impressive: The rate constant increased by almost ten orders of magnitude (10^{10}).

But of course you have to find a catalyst, which can take years at great cost.

- A. So instead, let's run the uncatalyzed reaction at double the temperature to 200°C .

1. Why is this not really “doubling” the temperature?
2. Calculate the rate constant at 200°C for the WGS reaction with no catalyst.

- B. On the original exam you were asked:

Assume that you start with an initial CO pressure of 0.100 atm. How long will it take for the pressure of CO to decrease to 0.010 atm?

given that the experimental rate law for the uncatalyzed reaction is

$$-\frac{\Delta[\text{CO}]}{\Delta t} = k[\text{CO}] \quad \text{where} \quad k = 7.0 \times 10^{-14} \text{ s}^{-1} \text{ at } 100^\circ\text{C}.$$

The first-order concentration-time equation gave the following result:

Many of us, however, approached the problem by plugging the knowns into the rate law and solving for the time when $[\text{CO}] = 0.010 \text{ atm}$, generally along the lines as shown below.

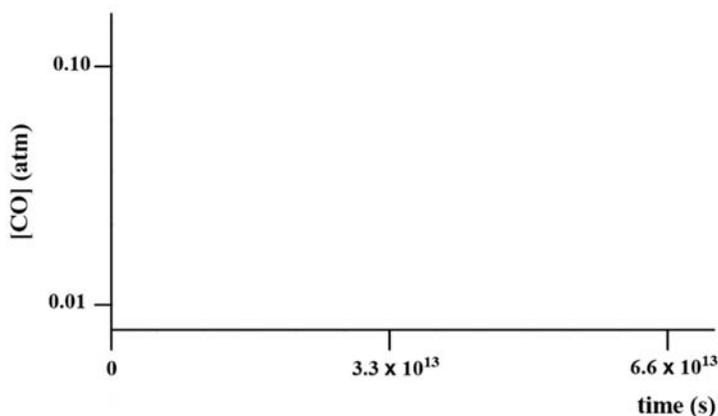
There are a few problem associated with this approach, including the implicit assumption that the rate of the reaction does not change with time. This approach is more like finding the **average** rate of the reaction over the concentration range 0.100 atm to 0.010 atm.

But since taking Exam Two we have talked about a type of kinetics where **the rate does not change** over the course of the reaction: **zero-order kinetics**.

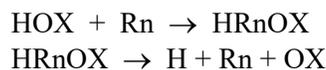
On the coordinate axes given below, draw and label plots of $[\text{CO}]$ versus time for the reaction assuming:

- (1) first-order kinetics, and
- (2) zero-order kinetics.

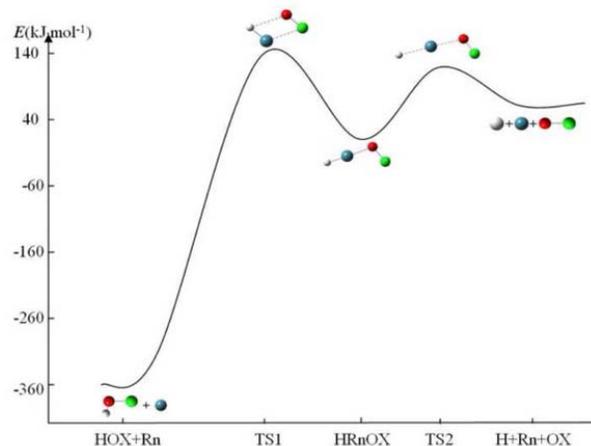
(Rough sketches are fine, but both plots should pass through the point where $[\text{CO}] = 0.01 \text{ atm}$ at $3.3 \times 10^{13} \text{ s}$.)



15. (**Ex2, Sp12**) A theoretical study of the insertion of radon into hypohalous acids (HOX, where X is Cl, Br, or I) was recently reported (*Inorg. Chim. Acta*, 2012; <http://dx.doi.org/10.1016/j.ica.2012.02.007>). The basic mechanism consists of two steps:



All species are in the gas phase, and the arrows in the reactions are generic; in other words, the steps may or may not be rapid equilibrium reactions. A potential energy profile for the mechanism is given on the right.



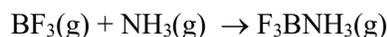
<http://www.sciencedirect.com/science/article/pii/S0020169312001107>

- What is the overall reaction?
- Is the overall reaction endothermic or exothermic?
- Which step is the rate determining step?

Why did you select this step as the rate determining step?

- Which steps, if any, correspond to rapid equilibria?
- Are there any intermediates in this mechanism? If so, list all of the intermediates.
- What is the expected rate law for this reaction?

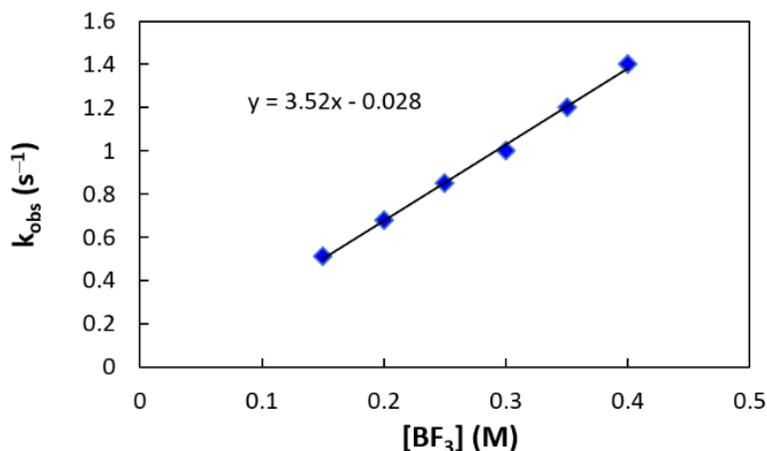
16. The gas-phase Lewis acid-base reaction



is first order in both reactants. The following data set was obtained under conditions of excess $[\text{BF}_3]$:

$[\text{BF}_3]$ (M)	k_{obs} (s^{-1})
0.15	0.51
0.20	0.68
0.25	0.85
0.30	1.0
0.35	1.2
0.40	1.4

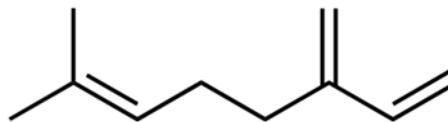
Determine the second-order rate constant for this reaction.



16.1 Another Pseudo-First-Order Kinetics Problem...

The kinetics of the gas phase reaction between NO_2 and conjugated alkenes (hydrocarbon compounds with at least two carbon-carbon double bonds separated by one carbon-carbon single bond) has been reported: *J. Phys. Chem. A* **2013**, *117*, 14132–14140.

A. One of the conjugated alkenes used in this study was myrcene, a natural organic compound found in many flavoring agents. A line drawing representing myrcene is shown on the right.



Write the chemical formula (C_xH_y) for myrcene.

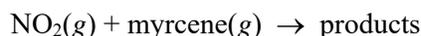
B. The study cited above used the concentration molecule/ cm^3 , which is a relatively common unit for gas phase kinetics. Convert this unit to mol/L:

$$1 \text{ molecule/cm}^3 = \underline{\hspace{2cm}} \text{ mol/L}$$

C. The following data were obtained at 298 K, where k_{obs} is the pseudo-first-order rate constant obtained for the concentrations in that row:

$[\text{NO}_2]_0$ ($\times 10^{15}$ molecule/ cm^3)	$[\text{myrcene}]_0$ ($\times 10^{13}$ molecule/ cm^3)	k_{obs} ($\times 10^{-4}$ s $^{-1}$)
0.48	2.9	1.10
1.00	5.9	1.75
1.26	2.5	2.58
1.72	7.1	3.78
1.74	4.2	3.87
2.81	12.8	6.30
2.76	8.9	6.84

Determine the second-order rate constant for the reaction between NO_2 and myrcene. In other words, for the reaction



with

$$\text{rate} = -\frac{\Delta[\text{myrcene}]}{\Delta t} = k[\text{NO}_2][\text{myrcene}]$$

determine k , and be sure to include the correct units.

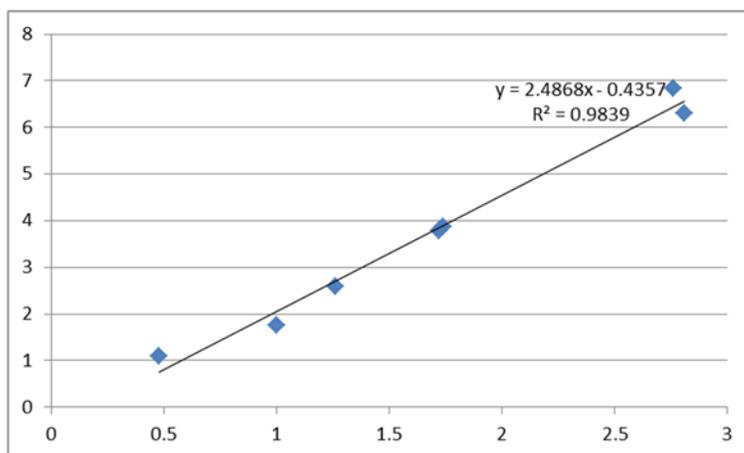
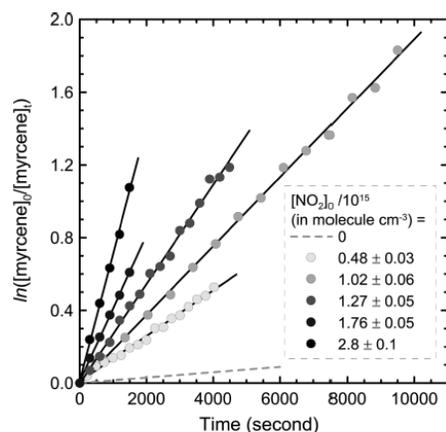


Figure 1. Pseudo-first-order experiments from the NO_2 -initiated reaction of myrcene.

17. (**Ex2, Sp2020**) In 2016, Nature reported the discovery of a small molecule (GS-5734) that exhibited antiviral activity against the Ebola virus in rhesus monkeys (*Nature*, **2016**, 531, 381–385). That drug, now called remdesivir, is drawing renewed attention as a possible treatment for COVID-19.

In the original study, the drug was administered by intravenous injection, 10 mg of GS-5734 per kg body weight of the rhesus monkey.

- A. What's the typical body weight of a rhesus monkey? _____

Cite your source for the above answer: _____

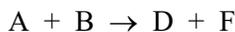
So, in this study, how much GS-5734 (in mg) would they have injected into that monkey?

- B. The study established a short half-life ($t_{1/2} = 0.39$ hr) for the elimination of GS-5734 from the blood stream. Assuming first-order kinetics, determine the rate constant for elimination of GS-5734 from the blood plasma in rhesus monkeys. Show your work and be sure to include the correct units in your answer.
- C. One subject in the study received an initial GS-5734 dose of 68 mg.
1. Assume the minimum effective amount of GS-5734 was known to be 41 mg. How long would it take for the GS-5734 in the subject's blood plasma to drop from 68 mg to 41 mg?
 2. How much GS-5734 (in mg) would still be in the subject's blood plasma after three half-lives? Show your work or explain your reasoning.
 3. How long would it take for GS-5734 to be "essentially gone" from the subject's blood plasma? Show your work or explain your reasoning.
- D. What if the elimination of GS-5734 from blood plasma followed zero-order kinetics instead of first-order kinetics. Can still determine the rate constant? If so, determine the rate constant. If not, why not?

18. (**Ex2, Sp2020**) It is likely that remdesivir (GS-5734 in the previous problem) will not turn out to be effective against COVID-19. Very few drugs in trial studies make it through to therapeutic use.

Perhaps another research group will find a "natural product" that is effective against COVID-19. Natural products are biological molecules that are often synthetic targets of organic chemists. If a natural product is found to treat COVID-19, someone will need to find a way to synthesize large amounts of the compound... and find it fast! Besides saving the world, that person will become obscenely wealthy. That person is... you.

Because your work is proprietary, you use labels instead of chemical formulas. Your one-step (show off) synthesis of the drug, D, found to be effective against COVID-19 is represented by the chemical equation shown below.

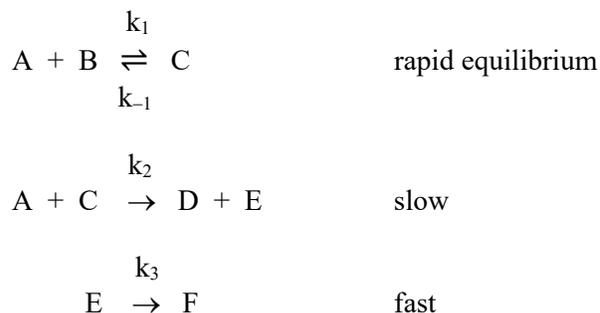


All reactants and products are in solution. A kinetic study of the reaction yielded the data shown below.

Exp	[A] (M)	[B] (M)	rate (M/s)
1	0.15	0.15	4.3×10^{-5}
2	0.15	0.60	17.2×10^{-5}
3	0.45	0.15	38.7×10^{-5}

- A. Determine the experimental rate law for the reaction.

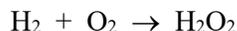
- B. Determine the rate constant and be sure to include units.
- C. What would be the rate of the reaction when $[A] = 0.35 M$ and $[B] = 0.25 M$?
- D. Consider this question before answering: If you increased the temperature, would the rate of the reaction increase, decrease, or stay the same?
If you can answer the question, write down your answer and explain your reasoning.
If you cannot answer, what else do you need to know, and why do you need to know it?
- E. The following mechanism was proposed for your life-saving money-making reaction.



Derive the theoretical rate law for this mechanism. Be sure to include the work showing how you derived the rate law.

Is the rate law for this mechanism consistent with the experimental rate law?

19. (**Ex2, Sp2017**) We considered the decomposition of hydrogen peroxide (H_2O_2) in class, but the reaction to synthesize hydrogen peroxide is arguably more important given its use as a chlorine-free oxidizing agent. The dominate method for producing H_2O_2 involves oxidation by anthraquinone, an energy-intensive and expensive process. A direct synthesis of hydrogen peroxide from hydrogen and oxygen is an attractive alternative



and the mechanism for this reaction catalyzed by palladium clusters was reported last year in the *Journal of the American Chemical Society* (JACS). (See: www.sciencedaily.com/releases/2016/01/160120201326.htm)

- A. The rate of formation of H_2O_2 increased with increasing pressure of $H_2(g)$, as shown in the table on the right. The JACS paper states that the H_2O_2 formation rates did not depend on O_2 pressure.

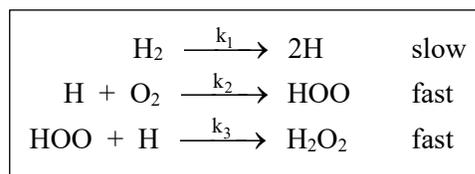
$[H_2]$ (kPa)	$\Delta[H_2O_2]/\Delta t$ (mol/s)
50	0.15
100	0.30

Write the experimental rate law for the reaction.

- B. The mechanism proposed in the JACS paper is fairly complicated, consisting of 12 consecutive reactions.

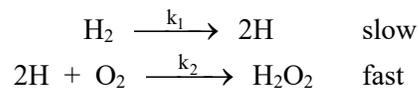
1. For the purpose of this problem, let's keep the first reaction and combine the other 11 into two reactions. The resulting three-step mechanism is shown on the right.

Write the theoretical rate law based on this mechanism.



Does it agree with the experimental rate law you determined in Part A? _____

2. We could have simplified this mechanism even further by combining the 11 reactions after the first step into one reaction, as shown on the right.



Write the theoretical rate law based on this mechanism.

3. Which of these mechanisms is more reasonable? _____

Explain your reasoning.

- C. The kinetic study revealed that the activation energy depended on the size of the palladium clusters. For 0.7 nm clusters, the activation energy was determined to be 9 kJ/mol, but for the 7 nm clusters, the activation energy increased to 14 kJ/mol.

1. For which catalyst will the reaction to form H_2O_2 be faster, 0.7 nm or 7 nm? _____

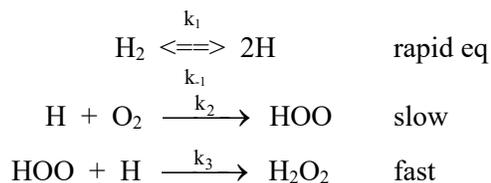
Explain your reasoning.

2. The rate constant at 4°C for the 0.7 nm catalyst was determined to be $1.3 \times 10^{-3} \text{ s}^{-1}$. What would the rate constant be at 4°C for the 7 nm catalyst? ***Be sure you show your work clearly. Most of the points on Part C.2 will come from how you set up the problem and whether or not you plugged the right values into the right places in the equation.***

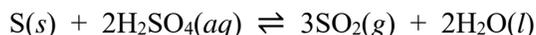
- D. Let's try one more mechanism, shown on the right.

Write the theoretical rate law based on this mechanism.

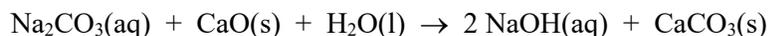
Does it agree with the experimental rate law you determined in Part A?



20. (Ex3, Su2011) Write the equilibrium expression for the chemical equation shown below.

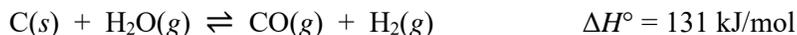


21. (Ex2, Su2009) Sodium hydroxide is an important compound. It is generally prepared by electrolysis of salt water, but another means of producing NaOH involves the following reaction:



Write an equilibrium constant expression for this reaction.

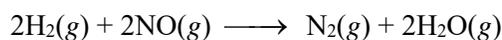
22. (Ex2, Sp2012) Consider the equilibrium process:



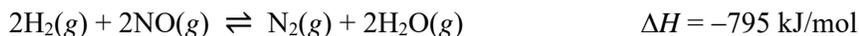
Predict the direction the equilibrium shifts (circle one) as a result of

- | | | | |
|---|----------------|----------------|-----------|
| A. adding $\text{H}_2(g)$. | left/reactants | right/products | no change |
| B. removing $\text{H}_2\text{O}(g)$.
(by adding a drying agent) | left/reactants | right/products | no change |
| C. removing some of the $\text{C}(s)$. | left/reactants | right/products | no change |
| D. removing all of the $\text{C}(s)$. | left/reactants | right/products | no change |
| E. increasing the temperature. | left/reactants | right/products | no change |
| F. increasing the pressure.
(by adding an inert gas) | left/reactants | right/products | no change |
| G. increasing the pressure.
(by decreasing the volume) | left/reactants | right/products | no change |

23. (Ex2, Sp2015) In recitation we considered the kinetics of the reaction



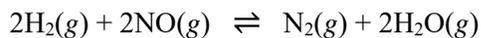
Now let's consider this reaction as an equilibrium process.



- A. Write the equilibrium expression for the above reaction.
- B. For each of the following, state whether the equilibrium distribution would shift to the left (more reactants), shift to the right (more products), or stay the same.

1. add $\text{N}_2(\text{g})$ _____
2. remove $\text{H}_2(\text{g})$ _____
3. increase the pressure
(by reducing the size of the container) _____
4. increase the pressure
(by adding $\text{Ne}(\text{g})$ to the container) _____
5. decrease the temperature _____

- C. Suppose 0.10 mol of NO and 0.10 mol of H_2 were placed in a 1.0-L vessel and heated at 1000°C until equilibrium was established. Set up the equation you would solve to find the concentrations at equilibrium assuming $K_c = 650$. You do not have to solve this equation!



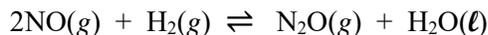
initial

(change)

equilibrium #

Write the equation in this box.

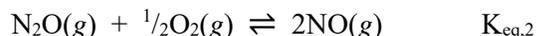
24. (Ex2, Sp'16) Now let's consider the overall reaction as an equilibrium process, carried out at a lower temperature such that H_2O is obtained as a liquid.



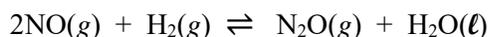
- A. Write the equilibrium expression for this reaction.
- B. For each of the following, state whether the equilibrium distribution would shift to the left (more reactants), shift to the right (more products), or stay the same.

1. add $\text{N}_2(\text{g})$ _____
2. remove $\text{H}_2(\text{g})$ _____
3. add $\text{N}_2\text{O}(\text{g})$ _____
4. remove $\text{H}_2\text{O}(\ell)$ _____
5. increase pressure by
decreasing the volume _____

- C. If we reduce the temperature even further, the equilibrium shifts to the right (more products, less reactants). Is this reaction endothermic or exothermic?
- D. I could not find the equilibrium constant for this reaction. Later in the course we will be able to calculate it from thermodynamic parameters, but for now if we want this value, we need to get it some other way. We should be able to find the equilibrium constants for these reactions:

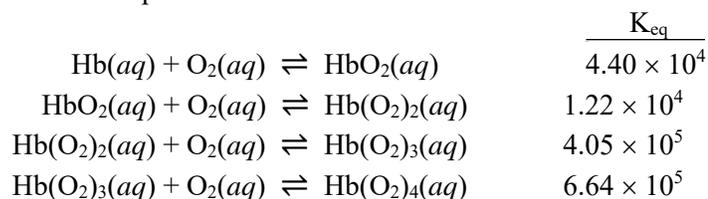


Show how you could use these equilibrium equations to determine the equilibrium constant for



Write the equilibrium constant in terms of $K_{\text{eq},1}$ and $K_{\text{eq},2}$. Be sure to show your work so we can see how you manipulated the first two equilibrium equations to get the third one.

25. (*Ex2, Sp2014*) We discussed two possible behaviors for sequential reactions: the common **Burger King Whopper Effect**, where the next reaction is less favored than the previous one; and the unusual ~~Lay's~~ **Cape Cod Potato Chip Effect**, where the next reaction is even more favored than the previous one. The stepwise bonding of oxygen to hemoglobin, Hb, follows the latter principle, and this behavior is called “cooperativity.” Let’s see if the equilibrium constants given below support the statement that the bonding of oxygen to hemoglobin exhibits a cooperative effect.

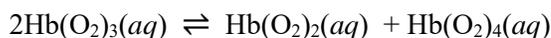


- A. Is the binding of the next oxygen molecule to hemoglobin always more favored than the binding of the previous oxygen molecule? If so, explain your reasoning. If not, what is(are) the exception(s)?
- B. The purpose of hemoglobin is to transport oxygen from the lungs to other parts of the body. If the hemoglobin is fully oxygenated in the lungs, then releasing all four of the oxygen molecules it carries would correspond to the following chemical equation:



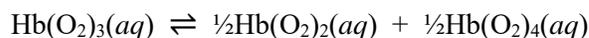
What is the value of the equilibrium constant for this reaction?

- C. Another type of reaction that indicates “Cape Cod Potato Chip” behavior is **disproportionation**, where a chemical species reacts with itself to give the previous and next species in the sequence, as illustrated below for $\text{Hb}(\text{O}_2)_3$.



Determine the value of the equilibrium constant for the disproportionation of $\text{Hb}(\text{O}_2)_3$ as written above.

How would K_{eq} change if the equilibrium was written as shown below?



26. (*Ex2, Sp2014*) Whenever I mention the “six official FSU strong acids” in class for the first time, a contingent of the class will come down at the end of the lecture (often carrying torches and pitchforks) to point out that chloric acid, $\text{HClO}_3(aq)$ is also a strong acid. Fair enough – let’s take a look.
- A. What are the six strong acids? You can either name them or give their formulas.

- B. I also told you on the first day of class that everything I will tell you this semester is wrong (at some level). There are more than six strong acids, and many folks consider chloric acid, $\text{HClO}_3(aq)$, to be a strong acid. Making that assumption, calculate the pH of $4.0 \times 10^{-2} M \text{HClO}_3(aq)$. [Note: Last year I added chloric acid to the list. This question is from Spring 2014.]
- C. But chlorous acid, $\text{HClO}_2(aq)$, is a weak acid, with $K_a = 1.1 \times 10^{-2}$.
- Do you expect the pH of $4.0 \times 10^{-2} M \text{HClO}_2(aq)$ to be greater or less than the pH of $4.0 \times 10^{-2} M \text{HClO}_3(aq)$?
Explain your reasoning.
 - Now, calculate the pH of $4.0 \times 10^{-2} M \text{HClO}_2(aq)$.
Does your answer agree with your prediction?
- D. If you solved part C using the quadratic equation and did not make any mistakes, you got the right answer. But if you used the approximation we have been using in class, then your answer may be slightly off. That's okay – you'll receive full credit for part C if it is otherwise correct – but why doesn't the approximation work as well in the above calculation? (You should answer part D regardless of how you worked part C.)

27. (Ex2, Fa2012) Acids and Bases

- A. Identify the following compounds as strong acids, weak acids, strong bases, weak bases, or essentially neutral when dissolved in water.

- NaNO_3 _____
- HNO_3 _____
- HNO_2 _____
- KNO_2 _____
- NH_4Cl _____

- B. Determine the pH of the solutions given below.

- 0.003 M $\text{H}_2\text{SO}_4(aq)$
- $7.6 \times 10^{-4} M \text{Ba}(\text{OH})_2(aq)$

28. (Ex2, Sp2015) Trimethylamine, $\text{N}(\text{CH}_3)_3$, is the gas responsible for the “fishy smell” as seafood starts to go bad, but when dissolved in water it acts as a weak base.*

- A. Write a chemical equation showing how $\text{N}(\text{CH}_3)_3$ acts as a weak base in water.

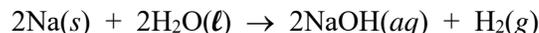
Write an equilibrium expression for that chemical equation.

- B. Determine the pH of 0.25 M $\text{N}(\text{CH}_3)_3(aq)$. K_b for trimethylamine is 6.3×10^{-5} .

*Greenland sharks contain high levels of the oxidized form of trimethylamine, $\text{ON}(\text{CH}_3)_3$, trimethylamine oxide (TMAO). It helps regulate their osmotic pressure and also acts as a natural antifreeze. During digestion, TMAO breaks down into trimethylamine (TMA). TMA causes intestinal distress and neurological effects similar to extreme drunkenness. Eating too much can even lead to convulsions and death. Early settlers of Iceland and Greenland figured out a way around this. Greenland shark flesh can be eaten with no ill effects if it is prepared correctly: the meat must be buried in the ground for 6 to 12 weeks, exposing it to several cycles of freezing and thawing. After this the meat is hung up to dry for several months, and finally cut into bite-sized cubes. The end product, Hákarl, is a delicacy.

<http://www.wired.com/2014/02/creature-feature-10-fun-facts-greenland-shark>

29. (*Ex3, Sp2016*) In 1947, the US government disposed of 20,000 lb of surplus sodium metal *by dumping it in Lake Lenore* (Grant County, Washington). Sodium reacts with water according to the following chemical equation.



The volume of Lake Lenore is roughly 4.1×10^{10} L. Assuming that the water in Lake Lenore was essentially pure in 1947, calculate the pH of the lake water after all the sodium reacts and the products are evenly distributed.

30. (*Ex2, Fa2012*) For each of the following salts, write the cation and the anion (*do not forget to include the charges*), indicate whether the solution would be acidic, basic, or neutral, and clearly explain your reasoning:

A. $(\text{CH}_3)_2\text{NH}_2\text{Cl}$

cation:	anion:	circle one: acidic basic neutral
explain your reasoning		

B. KBrO

cation:	anion:	circle one: acidic basic neutral
explain your reasoning		

C. NaHSO_3

cation:	anion:	circle one: acidic basic neutral
explain your reasoning		

D. $\text{Cr}(\text{NO}_3)_3$

cation:	anion:	circle one: acidic basic neutral
explain your reasoning		