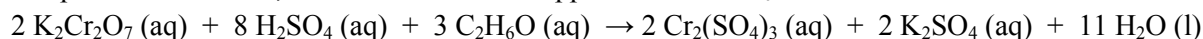


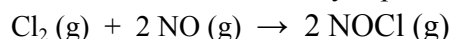
## CHM152 – Chapter 12: Chemical Kinetics – Homework

1. The reaction that occurs in a breathalyzer is given below. If the rate of appearance of  $\text{Cr}_2(\text{SO}_4)_3$  is 1.24 mol/min at a particular moment, what is the rate of disappearance of  $\text{C}_2\text{H}_6\text{O}$  at that moment?



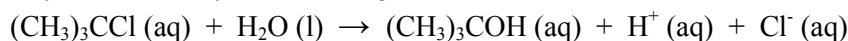
1.86 mol / min

2. Write the rate law for the reaction below without any experimental data.



Rate =  $k[\text{Cl}_2]^x[\text{NO}]^y$

3. The hydrolysis of tert-butyl chloride is given in the reaction below:



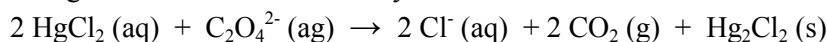
If the rate law is: rate =  $k[(\text{CH}_3)_3\text{CCl}]$ , what is the order of the reaction with respect to water?

Zero order wrt water since it is not part of the rate law

4. What is the overall order of the reaction that has the rate law: rate =  $k[\text{H}_2][\text{NO}]^2$ ?

Third Order

5. The following set of data was obtained by the method of initial rates for the reaction:



What is the rate law for the reaction? What is the value of the rate constant? What is the overall order?

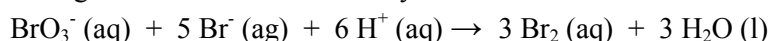
$[\text{HgCl}_2], \text{M}$	$[\text{C}_2\text{O}_4^{2-}], \text{M}$	Rate, M/s
0.10	0.10	$1.3 \times 10^{-7}$
0.10	0.20	$5.2 \times 10^{-7}$
0.20	0.20	$1.0 \times 10^{-6}$

Rate =  $k[\text{HgCl}_2][\text{C}_2\text{O}_4^{2-}]^2$

$k = 1.3 \times 10^{-4} \text{M}^{-2}\text{s}^{-1}$

overall order is third order

6. The following set of data was obtained by the method of initial rates for the reaction:



What is the rate law for the reaction? What is the value of the rate constant? What is the overall order?

Expt	$[\text{BrO}_3^-], \text{M}$	$[\text{Br}^-], \text{M}$	$[\text{H}^+], \text{M}$	Rate, M/s
1	0.10	0.10	0.10	$8.0 \times 10^{-4}$
2	0.20	0.10	0.10	$1.6 \times 10^{-3}$
3	0.20	0.15	0.10	$2.4 \times 10^{-3}$
4	0.10	0.10	0.25	$5.0 \times 10^{-3}$

Rate =  $k[\text{BrO}_3^-][\text{Br}^-][\text{H}^+]^2$   $k = 8.0 \text{M}^{-3}\text{s}^{-1}$  order = fourth

7. For a particular first order reaction, it takes 48 minutes for the concentration of the reactant to decrease to 25% of its initial value. What is the value for the rate constant (in  $s^{-1}$ ) for the reaction?  
 $\ln(25/100) = -k(48 \text{ min})(60 \text{ s/min}) \quad k = 4.8 \times 10^{-4} s^{-1}$
8. The rate constant for a first order reaction is equal to  $4.2 \times 10^{-4} s^{-1}$ . What is the half-life for the reaction?  
 $t_{1/2} = 0.693 / k \quad 0.693 / 4.2 \times 10^{-4} s^{-1} = 1.7 \times 10^3 \text{ seconds}$
9. A plot of  $1 / [BrO^-]$  vs. time is linear for the reaction:  $3 BrO^-(aq) \rightarrow BrO_3^-(aq) + 2 Br^-(aq)$   
 What is the order of the reaction with respect to the hypobromite ion?  
**Second order**
10. Nitrogen dioxide decomposes at  $300^\circ C$  via a second order process to produce nitrogen monoxide and oxygen gas. A sample of  $NO_2(g)$  is initially placed in a 2.50 L reaction vessel at  $300^\circ C$ . If the half-life and rate constant at  $300^\circ C$  are 11 seconds and  $0.54 M^{-1} s^{-1}$ , respectively, how many moles of  $NO_2$  were in the original sample?  
**0.42 mol**
11. Which statement about the half-life of a second order reaction is true?  
 a. Each half-life is half as long as the preceding one.  
**b. Each half-life is twice as long as the preceding one.**  
 c. Each half-life is four times as long as the preceding one.  
 d. The length of the half-life remains unchanged throughout the course of the reaction.
12. Which statement about the half-life of a zero order reaction is true?  
**a. Each half-life is half as long as the preceding one.**  
 b. Each half-life is twice as long as the preceding one.  
 c. Each half-life is four times as long as the preceding one.  
 d. The length of the half-life remains unchanged throughout the course of the reaction.
13. What percentage of a sample would remain after 8 half lives?
14. The elementary reaction:  $2 HI \rightarrow H_2 + I_2$ , is an example of a \_\_\_\_\_ reaction.  
 a. unimolecular  
**b. bimolecular**  
 c. termolecular  
 d. tetramolecular
15. A three-step mechanism has been suggested for the formation of carbonyl chloride:  
 Step 1:  $Cl_2 \rightarrow 2 Cl$  (fast, equilibrium)  
 Step 2:  $Cl + CO \rightarrow COCl$  (fast, equilibrium)  
 Step 3:  $COCl + Cl_2 \rightarrow COCl_2 + Cl$  (slow)  
 What is the rate-determining step? What is the molecularity of the rate-determining step?  
**Step 3 bimolecular**

16. For this reaction:  $2 \text{NO} (\text{g}) + \text{Cl}_2 (\text{g}) \rightarrow 2 \text{NOCl} (\text{g})$ , the real rate law is  $\text{rate} = k [\text{NO}][\text{Cl}_2]$   
 If the following steps are the mechanism, which one must be the rate determining step? step 1  
 What is the intermediate in this mechanism?  $\text{NOCl}_2$  What is the overall order? second  
 Step 1:  $\text{NO} (\text{g}) + \text{Cl}_2 (\text{g}) \rightarrow \text{NOCl}_2 (\text{g})$   
 Step 2:  $\text{NO} (\text{g}) + \text{NOCl}_2 (\text{g}) \rightarrow 2 \text{NOCl} (\text{g})$

17. What are three factors that affect the rate of a reaction?  
T, concentration, catalyst

18. The reaction for the decomposition of dinitrogen monoxide gas to form an oxygen radical is:  
 $\text{N}_2\text{O} (\text{g}) \rightarrow \text{N}_2 (\text{g}) + \text{O} (\text{g})$   
 If the activation energy is 250 kJ/mol and the frequency factor is  $8.0 \times 10^{11} \text{ s}^{-1}$ , what is the rate for the first order reaction at 1000 K?

$$\ln k = -(E_a/R)(1/T) + \ln A \text{ (frequency factor)} = 0.070 \text{ s}^{-1}$$

19. The aquation of tris(1, 10-phenanthroline)iron(II) in acid solution takes place according to the equation:  
 $\text{Fe}(\text{phen})_3^{2+} + 3 \text{H}_3\text{O}^+ + 3 \text{H}_2\text{O} \rightarrow \text{Fe}(\text{H}_2\text{O})_6^{2+} + 3 \text{phenH}^+$   
 If the activation energy is 126 kJ/mol and the rate constant at 30°C is  $9.8 \times 10^{-3} \text{ min}^{-1}$ , what is the rate constant at 50°C?  
 $0.217 \text{ min}^{-1}$

20. Consider the gas-phase hydration of hexafluoroacetone,  $(\text{CF}_3)_2\text{CO}$ :  
 $(\text{CF}_3)_2\text{CO} (\text{g}) + \text{H}_2\text{O} (\text{g}) \rightleftharpoons (\text{CF}_3)_2\text{C}(\text{OH})_2 (\text{g})$   
 At 76°C, the forward and reverse rate constants are  $k_f = 0.13 \text{ M}^{-1} \text{ s}^{-1}$  and  $k_r = 6.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}$ . What is the value of the equilibrium constant  $K_c$ ?  
 $K = \frac{0.13 \text{ M}^{-1} \text{ s}^{-1}}{6.2 \times 10^{-4} \text{ M}^{-1} \text{ s}^{-1}} \quad K = 210$