CH 222 Practice Problem Set #6

*This is a **practice problem set** and not the actual graded problem set that you will turn in for credit. Answers to each problem can be found at the end of this assignment.*

Covering: **Chapter Twelve, Chapter Twenty-one** *and* **Chapter Guide Six**
Important Tables and/or Constants: **R = 8.3145 J mol^{-1} K^{-1}**, "**Reaction Mechanisms Guide**" *(Handout)*

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1. Give the relative rates of disappearance of reactants and formation of products for each of the following reactions.
   a. $2\ O_3(g) \rightarrow 3\ O_2(g)$
   b. $2\ HOF(g) \rightarrow 2\ HF(g) + O_2(g)$
2. In the reaction $2\ O_3(g) \rightarrow 3\ O_2(g)$, the rate of formation of O_2 is 1.5×10^{-3} mol/L • s. What is the rate of decomposition of O_3?
3. The reaction between ozone and nitrogen dioxide at 231 K is first order in both NO_2 and O_3:
   $2\ NO_2(g) + O_3(g) \rightarrow N_2O_5(s) + O_2(g)$
   a. Write the rate equation for the reaction.
   b. If the concentration of NO_2 is tripled, what is the change in the reaction rate?
   c. What is the effect on reaction rate if the concentration of O_3 is halved?
4. The data in the table are for the reaction of NO and O_2 at 660 K.
   $2\ NO(g) + O_2(g) \rightarrow 2\ NO_2(g)$

Reactant Concentration (M)		
[NO]	**[O_2]**	**Rate of Disappearance of NO (M s^{-1})**
0.01	0.01	2.5×10^{-5}
0.02	0.01	1.0×10^{-4}
0.01	0.02	5.0×10^{-5}

   a. Determine the order of the reaction for each reactant.
   b. Write the rate equation for the reaction.
   c. Calculate the rate constant.
   d. Calculate the rate (in mol/L • s) at the instant when [NO] = 0.015 M and [O_2] = 0.0050 M
   e. At the instant when NO is reacting at the rate 1.0×10^{-4} mol/L • s, what is the rate at which O_2 is reacting and NO_2 is forming?
5. The rate equation for the hydrolysis of sucrose to fructose and glucose:
   $$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2\ C_6H_{12}O_6(aq)$$
   is "$-\Delta[\text{sucrose}]/\Delta t = k[C_{12}H_{22}O_{11}]$." After 2.57 h at 27 °C, the sucrose concentration decreased from 0.0146 M to 0.0132 M. Find the rate constant, *k*.
6. Ammonium cyanate, NH_4NCO, rearranges in water to give urea, $(NH_2)_2CO$:
   $$NH_4NCO(aq) \rightarrow (NH_2)_2CO(aq)$$
   The rate equation for this process is "Rate = $k[NH_4NCO]^2$" where k = 0.0113 L/mol • min. If the original concentration of NH_4NCO in solution is 0.229 mol/L, how long will it take for the concentration to decrease to 0.180 mol/L?

7. Hydrogen peroxide, $H_2O_2(aq)$, decomposes to $H_2O(l)$ and $O_2(g)$ in a reaction that is first order in H_2O_2 and has a rate constant $k = 1.06 \times 10^{-3}\ min^{-1}$.
   a. How long will it take for 15% of a sample of H_2O_2 to decompose?
   b. How long will it take for 85% of the sample to decompose?
8. The compound $Xe(CF3)_2$ decomposes in a first-order reaction to elemental Xe with a half-life of 30. min. If you place 7.50 mg of $Xe(CF_3)_2$ in a flask, how long must you wait until only 0.25 mg of $Xe(CF_3)_2$ remains?
9. Gaseous NO_2 decomposes at 573 K:

$$2\ NO_2(g) \rightarrow 2\ NO(g) + O_2(g)$$

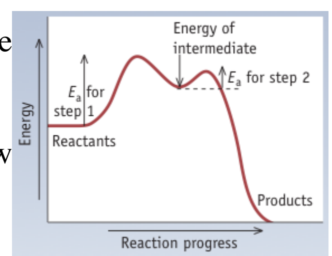
   The concentration of NO_2 was measured as a function of time. A graph of $1/[NO_2]$ versus time gives a straight line with a slope of 1.1 L/mol • s. What is the rate law for this reaction? What is the rate constant k?
10. Common sugar, sucrose, breaks down in dilute acid solution to form glucose and fructose. Both products have the same formula, $C_6H_{12}O_6$.

$$C_{12}H_{22}O_{11}(aq) + H_2O(l) \rightarrow 2\ C_6H_{12}O_6(aq)$$

   The rate of this reaction has been studied in acid solution, and the data in the table were obtained.

Time (min)	$[C_{12}H_{22}O_{11}]$ (M)
0	0.316
39	0.274
80	0.238
140	0.19
210	0.146

   a. Plot ln [sucrose] versus time and 1/[sucrose] versus time. What is the order of the reaction?
   b. Write the rate equation for the reaction, and calculate the rate constant, k.
   c. Estimate the concentration of sucrose after 175 min.
11. Answer the following questions based on the reaction coordinate diagram shown to the right.
   a. Is the reaction exothermic or endothermic?
   b. Does this reaction occur in more than one step? If so, how many?



12. What is the rate law for each of the following *elementary* reactions?
   a. $NO(g) + NO_3(g) \rightarrow 2\ NO_2(g)$
   b. $Cl(g) + H_2(g) \rightarrow HCl(g) + H(g)$
   c. $(CH_3)_3CBr(aq) \rightarrow (CH_3)_3C^+(aq) + Br^-(aq)$

13. Iodide ion is oxidized in acid solution by hydrogen peroxide:

$$H_2O_2(aq) + 2\ H^+(aq) + 2\ I^-(aq) \rightarrow I_2(aq) + 2\ H_2O(l)$$

A *proposed* mechanism is:

Step 1 *(slow)* $H_2O_2(aq) + I\text{-}(aq) \rightarrow H_2O(l) + OI^-(aq)$

Step 2 *(fast)* $H+(aq) + OI^-(aq) \rightarrow HOI(aq)$

Step 3 *(fast)* $HOI(aq) + H^+(aq) + I^-(aq) \rightarrow I_2(aq) + H_2O(l)$

a. Show that the three elementary steps add up to give the overall, stoichiometric equation.

b. What is the molecularity of each step?

c. For this mechanism to be consistent with kinetic data, what must be the experimental rate equation?

d. Identify any intermediates in the elementary steps in this reaction.

14. At temperatures below 500 K, the reaction between carbon monoxide and nitrogen dioxide

$$NO_2(g) + CO(g) \rightarrow CO_2(g) + NO(g)$$

has the following rate equation: **Rate =** $\boldsymbol{k[NO_2]^2}$ Which of the three mechanisms suggested below best agrees with the experimentally observed rate equation?

Mechanism 1 *Single, elementary step*

$NO_2 + CO \rightarrow CO_2 + NO$

Mechanism 2 *Two steps*

Slow $NO_2 + NO_2 \rightarrow NO_3 + NO$

Fast $NO_3 + CO \rightarrow NO_2 + CO_2$

Mechanism 3 *Two steps*

Slow $NO_2 \rightarrow NO + O$

Fast $CO + O \rightarrow CO_2$

T(K)	$\boldsymbol{k}$**(s^{-1})**
298	0.0409
308	0.0818
318	0.157

15. Data for the reaction $\mathbf{[Mn(CO)_5(CH_3CN)]^+ + NC_5H_5 \rightarrow [Mn(CO)_5(NC_5H_5)] + CH_3CN}$ are given in the table below. Calculate E_a from a plot of ln k versus 1/T.

16. Complete the following nuclear equations. Write the mass number and atomic number for the remaining particle, as well as its symbol.

a. ${}^{54}_{26}Fe + {}^{4}_{2}He \rightarrow 2\,{}^{1}_{0}n + ?$

b. ${}^{27}_{13}Al + {}^{4}_{2}He \rightarrow {}^{30}_{15}P + ?$

c. ${}^{32}_{16}S + {}^{1}_{0}n \rightarrow {}^{1}_{1}H + ?$

d. ${}^{96}_{42}Mo + {}^{2}_{1}H \rightarrow {}^{1}_{0}n + ?$

e. ${}^{98}_{42}Mo + {}^{1}_{0}n \rightarrow {}^{99}_{43}Tc + ?$

f. ${}^{18}_{9}F \rightarrow {}^{18}_{8}O + ?$

17. What particle is emitted in the following nuclear reactions? Write an equation for each reaction.
   a. Gold-198 decays to mercury-198.
   b. Radon-222 decays to polonium-218.
   c. Cesium-137 decays to barium-137.
   d. Indium-110 decays to cadmium-110.
18. Predict the probable mode of decay for each of the following radioactive isotopes, and write an equation to show the products of decay.
   a. Bromine-80m
   b. Californium-240
   c. Cobalt-61
   d. Carbon-11
19. Boron has two stable isotopes, ^{10}B and ^{11}B. Calculate the binding energies per nucleon of these two nuclei. The required masses (in grams per mole) are $^{1}_{1}H = 1.00783$, $^{1}_{0}n = 1.00867$, $^{10}B = 10.01294$, and $^{11}B = 11.00931$.
20. A three step mechanism for the reaction of $(CH_3)_3CBr$ and H_2O is proposed:

   Step 1 (slow) $(CH_3)_3CBr \rightarrow (CH_3)_3C^{+1} + Br^{-1}$

   Step 2 (fast) $(CH_3)_3C^{+1} + H_2O \rightarrow (CH_3)_3COH_2^{+1}$

   Step 3 (fast) $(CH_3)_3COH_2^{+1} + Br^{-1} \rightarrow (CH_3)_3COH + HBr$

   a. Write an equation for the overall reaction.
   b. Which step is rate determining?
   c. What rate law is expected for this reaction?
   d. What is the molecularity of each step?

Answers to the Practice Problem Set:

1. *Answers:*
   a. $-\frac{1}{2}\left(\frac{\Delta[O_3]}{\Delta t}\right) = \frac{1}{3}\left(\frac{\Delta[O_2]}{\Delta t}\right)$
   b. $-\frac{1}{2}\left(\frac{\Delta[HOF]}{\Delta t}\right) = \frac{1}{2}\left(\frac{\Delta[HF]}{\Delta t}\right) = \frac{\Delta[O_2]}{\Delta t}$
2. -1.0×10^{-3} mol/L • s
3. a. rate = $k[NO_2][O_3]$ b. rate triples c. rate halved
4. a. NO = 2nd order, O_2 = first order b. Rate = $k[NO]^2[O_2]$ c. k = 13 L^2/mol^2 • s d. 1.4×10^{-5} mol/L·s e. 5.0×10^{-5} mol/L·s (O_2), 1.0×10^{-4} mol/L·s (NO_2)
5. 0.0392 h^{-1}
6. 105 min (*note*: 2nd order kinetics!)
7. a. 153 min b. 1790 min
8. 150 min
9. rate = $k[NO_2]^2$ and k = 1.1 L/mol • s
10. a. first order b. k = 0.0037 min^{-1} c. 0.167 M
11. a. exothermic b. two steps
12. a) Rate = k[NO][NO_3] b) Rate = k[Cl][H_2] c) Rate = $k[(CH_3)_3CBr]$
13. a. (add equations together) b. bimolecular (steps 1 and 2) and termolecular (step 3) c. rate = $k[H_2O_2][I^{-1}]$ d. OI^- and HOI
14. Mechanism 2
15. y = -6373.3x + 18.19, r = -1 E_a = 53.0 kJ/mol
16. *Answers:*
    a. $^{56}_{28}Ni$ (d) $^{97}_{43}Tc$
    b. $^{1}_{0}n$ (e) $^{0}_{-1}\beta$
    c. $^{32}_{15}P$ (f) $^{0}_{+1}\beta$
17. *Answers:*
    a. $^{198}_{79}Au \rightarrow ^{198}_{80}Hg + ^{0}_{-1}\beta$
    b. $^{222}_{86}Rn \rightarrow ^{218}_{84}Po + ^{4}_{2}\alpha$
    c. $^{137}_{55}Cs \rightarrow ^{137}_{56}Ba + ^{0}_{-1}\beta$
    d. $^{110}_{49}In \rightarrow ^{110}_{48}Cd + ^{0}_{+1}\beta$
18. a. gamma decay b. alpha decay c. beta decay d. positron decay
19. For ^{10}B: 6.26×10^8 kJ/mol nucleons; for ^{11}B: 6.70×10^8 kJ/mol nucleons
20. a. $(CH_3)_3CBr + H_2O \rightarrow (CH_3)_3COH + HBr$ b. Step 1 c. Rate = $k[(CH_3)_3CBr]$ d. uni, bi, bi