Exam 4 Practice Problems

As always, these problems do not represent all the material covered for the exam. Be sure to go over the notes, the book, OWL, the workbook problems, and study guide in order to be prepared for all the material!

1. Consider the reaction

$2NH_3(g) \rightarrow N_2(g) + 3H_2(g)$

If the rate $\Delta[H_2]/\Delta t$ is 0.030 mol L^{-1} s^{-1}, then $-\Delta[NH_3]/\Delta t$ is

2. Consider the general reaction

$5Br^-(aq) + BrO_3^-(aq) + 6H^+(aq) \rightarrow 3Br_2(aq) + 3H_2O(l)$

For this reaction, the rate when expressed as $\Delta[Br_2]/\Delta t$ is the same as

A. $-\Delta[H_2O]/\Delta t$
B. $3\Delta[BrO_3^-]/\Delta t$
C. $-5\Delta[Br^-]/\Delta t$
D. $-0.6\Delta[Br^-]/\Delta t$
E. none of these choices is correct

3. For the reaction

$2A + B + 2C \rightarrow D + E$

the following initial rate data was collected at constant temperature. Determine the correct rate law for this reaction. All units are arbitrary.

Trial	[A]	[B]	[C]	Rate
1	0.225	0.150	0.350	0.0217
2	0.320	0.150	0.350	0.0439
3	0.225	0.250	0.350	0.0362
4	0.225	0.150	0.600	0.01270

4. What is the coordination number of cobalt in the complex ion $[Co(en)Cl_4]^-$?

5. In the compound $K[Co(C_2O_4)_2(H_2O)_2]$ what is the oxidation number and coordination number of cobalt?

6. Give the names for the following:
   a. $[Cu(NH_3)_4]Cl_2$.
   b. $K_3[Fe(CN)_6]$
   c. $[Co(H_2O)Cl_3]^-$.

7. Give the formulas for the following:
   a. pentaamminechlorocobalt(III) chloride

b. diamminedichloroethylenediaminecobalt(III) bromide
c. tetracyanonickelate(II)

8. $2NOBr(g) \rightarrow 2NO(g) + Br_2(g)$

[NOBr](mol L^{-1})	Rate (mol $L^{-1}s^{-1}$)
0.0450	1.62×10^{-3}
0.0310	7.69×10^{-4}
0.0095	7.22×10^{-5}

Based on the initial rate data above, what is the value of the rate constant?

9. Which of the following species could exist as isomers? Draw the isomers.

A. $[Co(H_2O)_4Cl_2]^+$

B. $[Pt(NH_3)Br_3]^-$

C. $[Pt(en)Cl_2]$

D. $[Pt(NH_3)_3Cl]^+$

10. Which of the following ion or ions do not have high spin or low spin states in an octahedral field of ligands? Explain.

A. Cr^{2+}

B. Mn^{4+}

C. Fe^{3+}

D. Co^{3+}

E. Ni^{2+}

11. What is the difference between a coordination compound and a complex ion?

12. Sucrose decomposes to fructose and glucose in acid solution. When ln [sucrose] is plotted vs. time, a straight line with slope of -0.208 hr^{-1} results.
    a. What is the rate law for the reaction?
    b. What is the half life?
    c. How long does it take for 82% of the sucrose to decompose?
13. The reaction $CH_3NC(g) \rightarrow CH_3CN(g)$ is first-order with respect to methyl isocyanide, CH_3NC. If it takes 10.3 minutes for exactly one quarter of the initial amount of methyl isocyanide to react, what is the rate constant in units of min^{-1}?

14. a. How can the formation of a complex ion be described in terms of a theory of acids and bases?
b. What is the essential requirement for a molecule or ion to act as a ligand?

15. The compound $Rh(CO)(H)(PH_3)_2$ forms *cis* and *trans* isomers. Use this information to predict the geometry of this complex, and draw the geometric isomers.

16. Ammonia will react with oxygen in the presence of a copper catalyst to form nitrogen and water. From 164.5°C to 179.0°C, the rate constant increases by a factor of 4.27. What is the activation energy (in kJ/mol) of this oxidation reaction?

17. The d_{xy} and the orbitals $d_{x^2 - y^2}$ both lie in the *xy* plane, yet for a metal ion in an octahedral complex the energy of the d_{xy} orbital is lower than that of the $d_{x^2 - y^2}$ orbital. Explain this using the arguments of crystal field theory.

18. a. Explain how the crystal field theory can use the magnitude of the splitting energy Δ to provide an explanation of the color and magnetic properties of octahedral complexes.
b. In promoting an electron from the t_{2g} set of orbitals to the e_g set, an octahedral complex absorbs a photon with a wavelength λ of 523 nm. Calculate the value of Δ in the complex, in kJ/mol. Given: $h = 6.626 \times 10^{-34}$ J s, $c = 2.998 \times 10^{8}$ m/s, and $N_a = 6.022 \times 10^{23}$ mol^{-1}

19. Consider the following mechanism for the oxidation of bromide ions by hydrogen peroxide in aqueous acid solution.

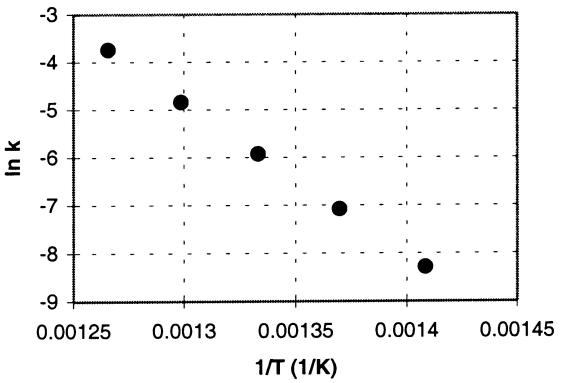
$H^+ + H_2O_2 \rightleftharpoons H_2O^+\text{-}OH$ (rapid equilibrium)
$H_2O^+\text{-}OH + Br^- \rightarrow HOBr + H_2O$ (slow)
$HOBr + H^+ + Br^- \rightarrow Br_2 + H_2O$ (fast)

Determine the rate law from the mechanism.

20. You are studying the rate of the reaction $2A \rightarrow B$ and have obtained measurements of the concentration of A at times *t* = 100, 200, 300, ..., 1000 seconds from the start of the reaction. Carefully describe how you would plot a graph and use it to:
a. prove that the reaction is second-order with respect to A.
b. determine the second-order rate constant *k*.

21. Cyclobutane decomposes to ethene in a first-order reaction. From measurements of the rate constant (*k*) at various absolute temperatures (*T*), the accompanying Arrhenius plot was obtained (ln *k* versus 1/*T*).

a. Calculate the energy of activation, E_a in kJ/mol.
b. Determine the value of the rate constant at 740. K. (In the plot, the units of *k* are s^{-1}.)



22. According to the collision theory of reaction rates, what are the three requirements which must be met before an elementary reaction between two molecules can occur?

23. The elementary reaction $HBr(g) + Br(g) \rightarrow H(g) + Br_2(g)$ is endothermic.

    a. Would you expect the rate constant for the back reaction to be smaller or larger than that for the forward reaction? Explain, briefly.
    b. Draw a fully-labeled reaction energy diagram for this reaction, showing the locations of the reactants, products and transition state.

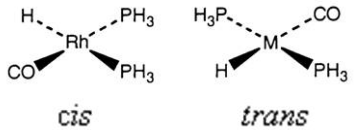
24. Briefly list the features/properties common to all catalysts and how they work. Draw a labeled reaction energy diagram as part of your answer.

ANSWERS:

1. 0.020 mol L^{-1} s^{-1}
2. D
3. Rate = $k[A]^2[B][C]^{-1}$
4. 6
5. CN = 6 and ON = +3
6. a. tetraamminecopper (II) chloride
   b. potassium hexacyanoferrate (III)
   c. aquatrichlorocobaltate (II)
7. a. $[Co(NH_3)_5Cl]Cl_2$
   b. $[Co(en)(NH_3)_2Cl_2]Br$ OR $[Co(NH_3)_2(en)Cl_2]$
   c. $[Ni(CN)_4]^{2-}$
8. 0.800 $M^{-1}s^{-1}$
9. A – Fac isomer and Mer isomer
10. B and E. Mn^{4+} and Ni^{2+}. Mn^{4+} has 2 d electrons, so it doesn't matter how large the Δ is; the electrons will be found in the t_{2g} orbitals. Ni^{2+} has 8 d electrons. Thus, it will have to fill the t_{2g} orbitals and have 2 electrons in the e_g orbitals no matter the splitting.
11. A coordination compound generally consists of a complex ion and a counter ion and is neutral overall; a complex ion has a central metal and surrounding ligands and it has a charge. It is not neutral
12. a. rate = k[sucrose]
    b. 3.33 hr

c. 8.24 hr

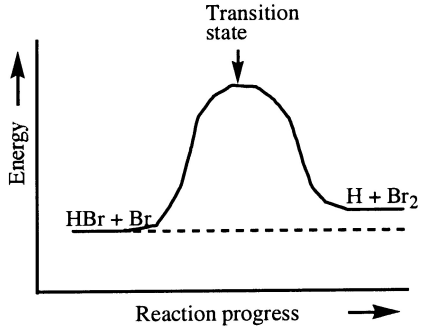
13. 0.0279 min^{-1}
14. a. According to Lewis, in an acid-base reaction, the acid accepts an electron pair from a base. Thus, in the formation of a metal-ligand complex, the metal is an acid and the ligand is a base.
    b. A ligand must have a lone pair of electrons available to donate in forming a bond with the metal
15. The complex has four ligands and there are geometric isomers; therefore it is square planar rather than tetrahedral.



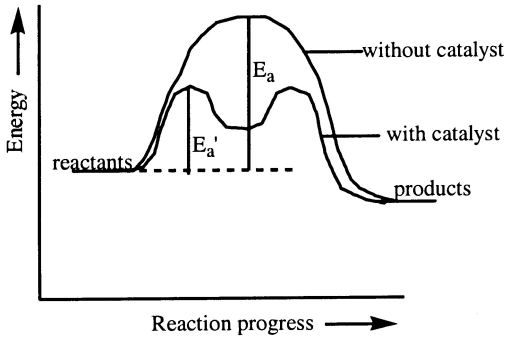
cis *trans*

16. 164.7 kJ/mol
17. The d_{xy} orbital lobes are directed between the *x* and *y* axes, whereas the $d_{x^2 - y^2}$ orbital lobes point along these axes. Thus, four ligands with their lone pairs, approaching the central atom along the + and - directions of the *x* and *y* axes will interact more strongly (repulsively) with electrons in the $d_{x^2 - y^2}$ orbital, raising it in energy above that of the d_{xy} orbital.
18. a. The energy needed for a photon to excite an electron from the lower to the higher set of the split *d* orbitals, will increase as Δ increases. This will mean the complex absorbs at shorter wavelengths, influencing its absorbed color and hence its transmitted color (the color opposite on the color wheel). The size of Δ also influences the number of unpaired electrons which affects the magnetic properties
    b. 229 kJ/mol
19. rate = $k_{obs}[H^+][H_2O_2][Br^-]$
20. a. Plot 1/[A] versus time. If a straight line results, the reaction is second-order.
    b. The rate constant *k* is the slope of the plot in (a).
21. a. 260 ± 20 kJ/mol (in other words, your answer should be between 240 and 280; it all depends on how you estimated those points on the graph)
    b. $\underline{2} \times 10^{-3}\ s^{-1}$
22. Molecules must collide with each other; the molecules must have sufficient energy to overcome the activation energy barrier; the molecules must have the correct orientation
23. Since the reaction is endothermic, its has a higher energy in the final state than in the initial state. Thus, the forward reaction requires a larger amount of energy to reach the transition state. Therefore, the k_{fwd} is larger. This is seen in the diagram below.

b.



24. Catalysts speed up a reaction by providing an alternative route of lower activation energy. They do not alter starting or ending potential energies of the reaction.


Energy
Reaction progress
reactants
products
E_a
E_a'
without catalyst
with catalyst