HOMEWORK 4A

1. Name the following complex ions.
   (a) Ni(CN)₄²⁻   (b) Cr(NH₃)₄Cl₂⁺   (c) Fe(C₂O₄)₃⁻   (d) Co(SCN)₂(H₂O)₄⁺

2. Give the formula for the following complex ions.
   (a) tetrachloroferrate(III)   (b) pentaamineaquaruthenium(III)
   (c) tetracarbonyldihydroxochromium(III)   (d) amminetrichloroplatanate(II)

3. Name the following coordination compounds.
   (a) [Cr(H₂O)₅Br]Br₂   (b) [Fe(NH₂CH₂CH₂NH₂)₂(NO₂)₂]Cl
   (c) Na₃[Co(CN)₆]   (d) [Pt(NH₃)₄I₂]SO₄

4. Identify each ligand as monodentate, bidentate, tridentate, etc.
   (a) CN⁻   (b) C₂O₄²⁻
   (c) NH₃   (d) H₂N(CH₂)₂NH₂ (ethylenediamine)

5. Draw and name all the geometrical isomers of Co(NH₃)₄(NO₂)₂

6. Draw all the geometrical isomers of Pt(CN)₂Br₂(H₂O)₂

7. Which one of the geometrical isomers in question 6 exhibit optical isomerism? Draw the two optical isomers.

HOMEWORK 4B

1. Write the complete formation reaction for each of the following complex ions.
   (a) Ni(CN)₄²⁻   (b) Mn(C₂O₄)₂²⁻

2. The complete formation constant for HgI₂⁻ is 1.0 x 10⁻³⁰. Calculate the concentration of Hg²⁺ ions in a solution that was originally 0.010 M Hg²⁺ and 0.78 M I⁻.

3. The copper (I) ion forms a chloride salt that has a K_sp = 1.2 x 10⁻⁶. Copper (I) also forms a complex ion with Cl⁻:
   \[ \text{Cu}^+(aq) + 2\text{Cl}^-(aq) \rightarrow \text{CuCl}_2^- (aq) \quad K_f = 8.7 \times 10^4 \]
   (a) Calculate the molar solubility of copper (I) chloride in pure water.
   (b) Calculate the molar solubility of copper (I) chloride in 0.10 M sodium chloride.
1. Draw the d-orbital splitting diagrams for the octahedral complex ions of each of the following, showing the correct number of d electrons, and identify each as paramagnetic or diamagnetic.
   (a) Cr$^{3+}$
   (b) Co$^{3+}$ (high and low spin)
   (c) Fe$^{3+}$ (high and low spin)
   (d) Zn$^{2+}$

2. Draw the expected d-orbital splitting for Pd$^{2+}$ assuming the following geometries, showing the correct number of d electrons, and predict which geometry would be the most stable.
   (a) octahedral
   (b) tetrahedral
   (c) square planar
   (d) linear

3. Identify each ligand as strong field-ligand or a weak-field ligand
   (a) O$^2$-
   (b) CO

4. Both NiCl$_4^{2-}$ and Ni(CN)$_4^{2-}$ have four ligands. The first complex ion is paramagnetic and the second is diamagnetic. Identify the complexes as either square planar or tetrahedral.

5. Answer the following concerning the complex ions hexacyanocobaltate(III) and hexachlorocobaltate(III)
   (a) give the formula of each complex ion
   (b) give the electron configuration of the cobalt ion in each
   (c) identify each ligand as strong-field or weak-field
   (d) draw the d-orbital splitting pattern for each the cobalt ion in each complex
   (e) identify the complex ion as paramagnetic or diamagnetic
   (f) identify the complex ion that produces a red solution, and the complex ion that produces a blue solution

6. The tetrabromocobaltate (II) ion absorbs electromagnetic radiation with a wavelength of 3.4 x 10$^{-6}$ m. Determine the splitting energy of the complex ion.

7. Identify the Lewis acid and Lewis base in each of the following reactions.
   (a) Cu$^{2+}$ (aq) + 4NH$_3$ (aq) ⇌ Cu(NH$_3$)$_4^{2+}$ (aq)
   (b) Fe$^{3+}$ (aq) + 6H$_2$O (aq) ⇌ Fe(H$_2$O)$_6^{3+}$ (aq)
   (c) BF$_3$ (g) + F$^-$ (aq) ⇌ BF$_4^-$ (aq)
   (d) SO$_3$ (g) + H$_2$O (l) ⇌ H$_2$SO$_4$ (aq)
1. If a combustion reaction is a thermodynamically spontaneous process, how does the paper of a book survive in contact with atmospheric oxygen?

2. The reaction: \( \text{N}_2 + 3\text{H}_2 \rightarrow 2\text{NH}_3 \) is first order in nitrogen concentration and second order in hydrogen concentration. Write the rate expression for this reaction.

3. For the reaction in question 2, if the initial reaction rate is 0.20 M \( \text{N}_2 / \text{min} \), what would be the initial reaction rate in M \( \text{H}_2 / \text{min} \) and M \( \text{NH}_3 / \text{min} \)?

4. For the gas phase reaction:
\[
2\text{NO} + \text{Cl}_2 \rightarrow 2\text{NOCl}
\]
the following data were collected at the same temperature

<table>
<thead>
<tr>
<th>Initial ( p_{\text{NO}} ) (atm)</th>
<th>Initial ( p_{\text{Cl}_2} ) (atm)</th>
<th>Initial Rate (atm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.50</td>
<td>0.50</td>
<td>5.0 \times 10^{-3}</td>
</tr>
<tr>
<td>1.0</td>
<td>1.0</td>
<td>4.0 \times 10^{-2}</td>
</tr>
<tr>
<td>0.50</td>
<td>1.0</td>
<td>1.0 \times 10^{-2}</td>
</tr>
</tbody>
</table>

Since the pressure of a gas is directly proportional to the concentration of gas, we can express the rate law for a gaseous reaction in terms of partial pressures.

(a) What is the rate expression for this reaction?
(b) What is the order of this reaction?
(c) Calculate the numerical value of the rate constant, with units.
(d) What will be the initial rate if the initial pressure of NO is 0.75 atm and the initial pressure of Cl\(_2\) is 0.75 atm?

5. For the reaction:
\[
2\text{NO} + \text{H}_2 \rightarrow \text{N}_2\text{O} + \text{H}_2\text{O}
\]
the following data were collected at the same temperature

<table>
<thead>
<tr>
<th>Initial [NO]</th>
<th>Initial [H(_2)]</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.20</td>
<td>0.74</td>
<td>1.44</td>
</tr>
<tr>
<td>1.20</td>
<td>0.37</td>
<td>0.72</td>
</tr>
<tr>
<td>0.60</td>
<td>0.37</td>
<td>0.18</td>
</tr>
</tbody>
</table>

(a) What is the rate expression for this reaction?
(b) What is the order of this reaction?
(c) Calculate the numerical value of the rate constant, with units.
(d) What will be the initial rate if the initial concentration of NO is 0.75 M and the initial concentration of H\(_2\) is 0.75 M?
1. For the decomposition of ammonia, the following data were measured.

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>0</th>
<th>1.00</th>
<th>2.00</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>2.000</td>
<td>1.993</td>
<td>1.987</td>
</tr>
</tbody>
</table>

For this first-order reaction, write the rate expression and calculate the rate constant, $k$.

2. The reaction: $\text{SO}_2\text{Cl}_2 \rightarrow \text{SO}_2 + \text{Cl}_2$ is a first order reaction with the rate constant $k = 2.2 \times 10^{-5}$ s$^{-1}$ at 320ºC. What fraction of SO$_2$Cl$_2$ is decomposed on heating at 320ºC for 90.0 minutes?

3. Given the following data for the reaction: $\text{trans-C}_2\text{H}_2\text{Cl}_2 \rightarrow \text{cis-C}_2\text{H}_2\text{Cl}_2$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>10</th>
<th>20</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Quantity (mol)</td>
<td>1.00</td>
<td>0.90</td>
<td>0.81</td>
<td>0.73</td>
</tr>
</tbody>
</table>

(a) What is the order of the reaction?

(b) Predict the quantity of the trans compound after 50 minutes.

(c) How long will it take half of the trans compound to decompose?

4. Given the following data for the reaction: $2\text{NO}_2 \rightarrow \text{N}_2\text{O}_4$

<table>
<thead>
<tr>
<th>Time (min)</th>
<th>0</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Concentration (M)</td>
<td>0.556</td>
<td>0.435</td>
<td>0.357</td>
<td>0.303</td>
<td>0.263</td>
</tr>
</tbody>
</table>

(a) What is the order of the reaction?

(b) Predict the concentration of NO$_2$ after 200. minutes.
1. The reaction

\[ 2\text{NO} + \text{F}_2 \rightarrow 2\text{ONF} \]

occurs via the 2-step mechanism

(1) \[ \text{NO} + \text{F}_2 \rightarrow \text{ONF} + \text{F} \] slow reaction, with rate constant \( k_1 \)
(2) \[ \text{NO} + \text{F} \rightarrow \text{ONF} \] fast reaction, with rate constant \( k_2 \)

Deduce the rate equation that agrees with this mechanism.

2. Assume that the reaction

\[ 5\text{Br}^- + \text{BrO}_3^- + 6\text{H}^+ \rightarrow 3\text{Br}_2 + \text{H}_2\text{O} \]

proceeds by the mechanism

(1) \[ 2\text{H}^+ + \text{BrO}_3^- \leftrightarrow \text{H}_2\text{BrO}_3^+ \] equilibrium, with equilibrium constant \( K_1 \)
(2) \[ \text{Br}^- + \text{H}_2\text{BrO}_3^+ \rightarrow \text{Br}^-\text{BrO}_2 + \text{H}_2\text{O} \] slow reaction, with rate constant \( k_2 \)
(3) \[ \text{Br}^-\text{BrO}_2 + 4\text{H}^+ + 4\text{Br}^- \rightarrow 3\text{Br}_2 + 2\text{H}_2\text{O} \] fast reaction, with rate constant \( k_3 \)

Deduce the rate equation that agrees with this mechanism.

3. What is the physical interpretation of \( E_a \)? Why should it have any bearing on rates of reactions?

4. If you knew \( E_a \) for the forward and reverse reactions, how could you use them to calculate \( \Delta H^\circ \)? Illustrate your answer with a diagram.

5. The fraction of molecules that have the sufficient energy to cross the activation barrier, \( E_a \), can be increase be either (1) making the molecules more energetic or (2) by lowering the barrier.

(a) Which are you doing when you raise the temperature? What potential disadvantages are there in this method?

(b) Which are you using when you add a catalyst? What does the catalyst do that makes this possible?

6. It is often said that, near room temperature, a reaction rate doubles if the temperature is increased by 10 Cº. Calculate the activation energy of a reaction whose rate exactly doubles between 27ºC and 37ºC.

7. The rate constant for the decomposition of \( \text{N}_2\text{O}_5 \) in carbon tetrachloride is \( 6.2 \times 10^{-4} \text{ s}^{-1} \) at 45ºC. Calculate the rate constant at 100.ºC if the activation energy is 103 kJ.
1. Define *Lewis acid* and *Lewis base*.

2. Identify each as a Lewis Acid or a Lewis base.
   - (a) Ni₃
   - (b) Bi₃
   - (c) Cl⁻
   - (d) Na⁺
   - (e) CN⁻
   - (f) S²⁻
   - (g) Mg²⁺
   - (h) NO₂⁻

3. Name the following complex ions.
   - (a) NiCl₆⁴⁻
   - (b) Co(NH₃)₅NO₂²⁺
   - (c) Fe(CN)₆(C₂O₄)₂³⁻
   - (d) PtF₂Cl₂Br₂²⁻

4. For each of the following coordination compounds, identify the (1) name, (2) coordination complex, (3) charge of the complex (4) ligand or ligands, with their charges if appropriate (5) coordination number of the metal, (6) counter ion, with their charges, and (7) oxidation number of the metal.
   - (a) [Cr(NH₃)₆]Br₂
   - (b) [Ir(NH₃)₃(NO₂)₃]
   - (c) K₂[PtCl₄]
   - (d) [Co(NH₃)₃]I₂

5. A certain metal ion, M²⁺, forms a complex ion with carbon monoxide molecules to form M(CO)ₓ²⁺. A Job Plot of absorbance as a function of mole fraction of ligand was obtained, and is shown below. Determine the formula for the complex ion.

![Graph showing Job Plot with equations y = 0.95x + 0.19 and y = -1.50x + 2.15]

6. Draw all the geometrical and optical isomers of Ru(en)₂BrCl

7. The overall formation constant for Fe(CN)₆³⁻ is 1.0 x 10¹². Calculate the concentration of Fe³⁺ ions in a solution that was originally 0.10 M Fe³⁺ and 1.0 M CN⁻.

8. Silver chloride has a Kₛₒₚ = 1.6 x 10⁻¹⁰, and diamminesilver(I) has a Kₜ = 1.7 x 10⁷
   (a) Calculate the molar solubility of silver chloride in pure water.
   (b) Calculate the molar solubility of silver chloride in 6.0 M ammonia.

*(continued on next page)*
9. Draw the expected d-orbital splitting for Ru\(^{2+}\) assuming the following geometries, and predict which geometry would be the most stable
   (a) octahedral   (b) tetrahedral   (c) square planar

10. Identify each ligand as strong field-ligand or a weak-field ligand
   (a) I\(^-\)  
   (b) CN\(^-\)

11. Answer the following concerning the complex ions hexanitritoferrate(II) and hexabromoferrate(II)
   (a) give the formula of each complex ion
   (b) give the electron configuration of the iron ion in each
   (c) identify each ligand as strong-field or weak-field
   (d) draw the d-orbital splitting pattern for each the iron ion in each complex
   (e) identify each complex ion as high-spin or low-spin
   (f) if the first complex has a splitting energy of 7.4 x 10\(^{-19}\) J, calculate the wavelength of electromagnetic radiation it will absorb
   (g) if the second complex ion has a splitting energy of 239 kJ/mol, calculate the wavelength of electromagnetic radiation it will absorb
   (h) determine which of the two complexes will be colored

12. For the reaction: \(2\text{NH}_3(g) \rightarrow \text{N}_2(g) + 3\text{H}_2(g)\)
    assuming the reaction vessel starts with only \(\text{NH}_3\), sketch how the concentrations of \(\text{NH}_3\), \(\text{N}_2\), and \(\text{H}_2\) change vs. time until the reaction reaches equilibrium.

13. For the reaction: \(X + Y \rightarrow Z\)
    the following data were collected at the same temperature
    \[
    \begin{array}{ccc}
    \text{Initial [X]} & \text{Initial [Y]} & \text{Initial Rate (M/s)} \\
    1.0 & 1.0 & 0.020 \\
    1.0 & 2.0 & 0.040 \\
    2.0 & 2.0 & 0.080 \\
    \end{array}
    \]
    (a) What is the rate expression for this reaction?
    (b) What is the order with respect to each reactant, and the overall order of this reaction?
    (c) Calculate the numerical value of the rate constant, with units.
    (d) What will be the initial rate if the initial concentration of \(X\) is 1.5 M and the initial concentration of \(Y\) is 2.5 M?

\(\text{(continued on next page)}\)
14. For the reaction: \( S + R \rightarrow F \)
the following data were collected at the same temperature

<table>
<thead>
<tr>
<th>Initial [S]</th>
<th>Initial [R]</th>
<th>Initial Rate (M/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.0</td>
<td>4.0</td>
<td>5.7</td>
</tr>
<tr>
<td>2.0</td>
<td>8.0</td>
<td>11.4</td>
</tr>
<tr>
<td>4.0</td>
<td>4.0</td>
<td>22.8</td>
</tr>
</tbody>
</table>

(a) What is the rate expression for this reaction?
(b) What is the order with respect to each reactant, and the overall order of this reaction?
(b) Calculate the numerical value of the rate constant, with units.
(c) What will be the initial rate if the initial concentration of \( S \) is 3.0 M and the initial concentration of \( R \) is 6.0 M?

15. For the reaction: \( A + B \rightarrow C \)
the following data were collected at the same temperature

<table>
<thead>
<tr>
<th>Initial [A]</th>
<th>Initial [B]</th>
<th>Initial Rate (M/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.003</td>
<td>0.005</td>
<td>( 2 \times 10^{-8} )</td>
</tr>
<tr>
<td>0.006</td>
<td>0.005</td>
<td>( 2 \times 10^{-8} )</td>
</tr>
<tr>
<td>0.003</td>
<td>0.010</td>
<td>( 8 \times 10^{-8} )</td>
</tr>
</tbody>
</table>

(a) What is the rate expression for this reaction?
(b) What is the order with respect to each reactant, and the overall order of this reaction?
(d) Calculate the numerical value of the rate constant, with units.
(e) What will be the initial rate if the initial concentration of \( A \) is 0.009 M and the initial concentration of \( B \) is 0.010 M?

16. Given the following data for the reaction: \( J \rightarrow K \)

<table>
<thead>
<tr>
<th>Time (min):</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. of J (M):</td>
<td>0.0333</td>
<td>0.0200</td>
<td>0.0143</td>
<td>0.0111</td>
</tr>
</tbody>
</table>

(a) What is the order of the reaction?
(b) Determine the value of the specific rate constant
(c) Predict the concentration of \( J \) remaining after 50. minutes.
(d) How long will it take half of \( J \) to react away?

17. Given the following data for the reaction: \( Q \rightarrow R \)

<table>
<thead>
<tr>
<th>Time (s):</th>
<th>0</th>
<th>20</th>
<th>40</th>
<th>60</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conc. of Q (M):</td>
<td>0.0724</td>
<td>0.0525</td>
<td>0.0380</td>
<td>0.0275</td>
<td>0.0200</td>
</tr>
</tbody>
</table>

(a) What is the order of the reaction?
(b) Determine the value of the specific rate constant
(c) Predict the concentration of \( Q \) after 100. seconds.
(d) How long will it take half of \( Q \) to react away?

(continued on next page)
18. Assume that the reaction: \( 2O_3 \rightarrow 3O_2 \) 
proceeds by the mechanism

(1) \( O_3 \rightleftharpoons O_2 + O \) equilibrium, with equilibrium constant \( K_1 \)

(2) \( O + O_3 \rightarrow 2O_2 \) slow reaction, with rate constant \( k_2 \)

(a) What is the molecularity of each step?
(b) Deduce the rate equation that agrees with this mechanism.

19. Assume that the reaction: \( Br_2 + SiHBr_3 \rightarrow HBr + SiBr_4 \) 
proceeds by the mechanism

(1) \( Br_2 \rightleftharpoons 2Br \) equilibrium, with equilibrium constant \( K_1 \)

(2) \( Br + SiHBr_3 \rightarrow HBr + SiBr_3 \) slow reaction, with rate constant \( k_2 \)

(3) \( Br + SiBr_3 \rightarrow SiBr_4 \) fast reaction, with rate constant \( k_3 \)

(a) What is the molecularity of each step?
(b) Deduce the rate equation that agrees with this mechanism.

20. List the assumptions of the collision theory for chemical reactions.

21. Identify the three factors that mathematically determine the numerical value of the specific rate constant.

22. A particular reaction has a rate constant of 0.0150 \( \text{M}^{-1}\text{s}^{-1} \) at 298 K and 0.0275 \( \text{M}^{-1}\text{s}^{-1} \) at 308 K. Calculate the activation energy of the reaction.

23. A reaction that has an enthalpy change of -125 kJ/mol and an activation energy of 225 kJ/mol.
   (a) Draw an energy profile for this reaction
   (b) Determine the enthalpy change and activation energy for the reverse reaction
   (c) Draw the energy profile for this reaction when a catalyst has been introduced.

**HOMEWORK 4R ANSWERS**

1. Lewis acid – electron pair acceptor
   Lewis base – electron pair donor

2. (a) base  (b) acid  (c) base  (d) acid
    (e) base  (f) base  (g) acid  (h) base

3. (a) hexachloronickelate(II)  (b) pentaaminenitricobalt(III)
   (c) dicyanobis(oxalato)ferrate(III)  (d) dibromodichlorodifluoroplatinate(IV)

(continued on next page)
4. (a) hexaamminechromium(II) bromide \[ \text{Cr(NH}_3)_6^{2+} \text{NH}_3 \text{Br}^- \text{Br}^- \]
(b) triamminetrimetritoirridium(III) \[ \text{Ir(NH}_3)_3(\text{NO}_2)_3 \text{NH}_3, \text{NO}_2^- \text{none} \text{3+} \]
(c) potassium tetrachloroplatanate(II) \[ \text{PtCl}_4^- \text{Cl}^- \text{4} \text{K}^+ \text{2+} \]
(d) pentaammineiodocobalt(III) iodide \[ \text{Co(NH}_3)_5\text{I}^{2+} \text{NH}_3, \text{I}^- \text{6} \text{I}^- \text{3+} \]

5. \[ \text{M(CO)}_4 \]

6. 

7. \[ 2.4 \times 10^{-41} \text{ M} \]

8. (a) \[ 1.3 \times 10^{-5} \text{ M} \]
(b) \[ 0.28 \text{ M} \]

9. (a) octahedral 
(b) tetrahedral 
(c) square planar

10. (a) weak 
(b) strong

11. (a) \[ \text{Fe(NO}_2)_6^{4-}, \text{FeBr}_6^{4-} \]
(b) for both: [Ar]3d
(c) \[ \text{NO}_2^- \text{strong, Br}^- \text{weak} \]
(d) 

(e) \[ \text{Fe(NO}_2)_6^{4-} \text{low-spin, FeBr}_6^{4-} \text{high-spin} \]
(f) \[ 2.7 \times 10^{-7} \text{ m} \]
(g) \[ 5.0 \times 10^{-7} \text{ m} \]
(h) \[ \text{FeBr}_6^{4-} \]

(continued on next page)
13. (a) Rate = \( k[X][Y] \)  
   (c) 0.020 M\(^{-1}\)s\(^{-1}\)  
   (e) 0.020 M\(^{-1}\)s\(^{-1}\)  
   (b) \( X = 1^{st}, Y = 1^{st}, \text{overall} = 2^{nd} \)  
   (d) 0.076 M/s

14. (a) Rate = \( k[S]^2[R] \)  
   (b) \( S = 2^{nd}, R = 1^{st}, \text{overall} = 3^{rd} \)  
   (c) 0.36 M\(^2\)min\(^{-1}\)  
   (d) 19 M/min

15. (a) Rate = \( k[B]^2 \)  
   (b) \( A = 0^{th}, B = 2^{nd}, \text{overall} = 2^{nd} \)  
   (c) \( 8 \times 10^{-4} \) M\(^{-1}\)s\(^{-1}\)  
   (d) \( 8 \times 10^{-8} \) M/s

16. (a) 2\(^{nd}\) order  
   (c) 0.012 M  
   (d) 30. min

17. (a) 1\(^{st}\) order  
   (c) 0.014 M  
   (d) 43 s

18. (a) 1, 2  
   (b) Rate = \( k[O_3]^2[O_2]^{-1} \)

19. (a) 1, 2, 2  
   (b) Rate = \( k[\text{SiHBr}_3][\text{Br}_2]^{\frac{1}{2}} \)

20. Molecules must collide to react, they must collide with sufficient energy, they must collide in the proper orientation

21. Collision frequency, fraction of collisions with the activation energy, fraction of collisions with the proper orientation

22. 46,000 J/mol

23. (a) 
   (b) \( \Delta H_{\text{rev}} = +125 \) kJ/mol, \( E_{\text{a,rev}} = 350 \) kJ/mol  
   (c) dotted line