1. (16 points) Acetylsalicylic acid, the molecule pictured here, is better known as aspirin.

Describing the bonding in aspirin, acetylsalicylic acid.

(a) The molecule has _______ sigma (σ) bonds and _______ pi (π) bonds.

(b) Estimate the values of the indicated angles:
    Angle A = _____    Angle B = _____    Angle C = _____    Angle D = _____

(c) The orbital hybridization scheme used by all the C atoms of the benzene ring (the C₆ ring) is _______

(d) Give hybridization of each of the following atoms:
    C1 = _____    O2 = _____    C3 = _____    C4 = _____

(e) Circle the shortest carbon-oxygen bonds on the drawing above.

If the pH of a 0.018 M solution of aspirin is 2.61, what is the hydronium ion concentration of the solution?

(a) 2.45 x 10⁻³ M

(b) 2.61 x 10⁻⁴ M

(c) 3.27 x 10⁻⁴ M

(d) 4.07 x 10⁻¹² M

Can the aspirin molecule form hydrogen bonds with water? Why or why not? Explain briefly.
2. (10 points) Nitric acid—structure, bonding, and chemistry

Fill in the remaining electrons in the nitric acid structure below and then answer the questions that follow.

\[
\text{H} - \text{O} - \text{N} - \text{O} - \text{O}
\]

The formal charge on the central N is _______ and its hybridization is __________. The formal charge on the O atom marked 1 is ____ and its hybridization is _________. The O—N—O angle is about _______ degrees, while the H—O—N is _______ degrees.

If you have a 0.015 M solution of nitric acid, its pH is about

(a) 1.50
(b) 1.83
(c) 7.00
(d) 12.18
(e) none of the above

3. (6 points) The formate ion, HCO\textsubscript{2}^-\textsuperscript{−}, is a common ion in natural systems.

\[
\text{\begin{array}{c}
\text{H} \\
\text{O} \\
\text{\textsuperscript{−}C \textsuperscript{−} O} \\
\end{array}} \quad \rightarrow \quad \text{\begin{array}{c}
\text{\textsuperscript{−}O \textsuperscript{−} C \textsuperscript{−} O} \\
\end{array}}
\]

i. What is the carbon-oxygen bond order? ____________

ii. What is the hybridization of the C atom? ______________

iii. Can the ion be attached to a water molecule via hydrogen bonding? ______________

iv. What is the pH of a 0.15 M solution of sodium formate, NaHCO\textsubscript{2}? 

(a) 3.75
(b) 5.54
(c) 8.46
(d) 10.25
4. (11 points) The chemistry of sulfur dioxide, SO₂, and sulfur trioxide, SO₃.

(a) Draw an electron dot structure for SO₂ and any appropriate resonance structures.

(b) The electron pair geometry (structural pair geometry) of the ion is ________________ and the molecular shape is ________________. The S atom hybridization is ____, and the O—S—O angle is ________________

(c) Gaseous SO₂ can be liquefied at –75 °C. What intermolecular force is responsible for the attraction between SO₂ molecules? ________________________________

(d) Sulfur dioxide burns in oxygen to give sulfur trioxide.

\[
\text{SO}_2(g) + \frac{1}{2} \text{O}_2(g) \rightarrow \text{SO}_3(g)
\]

Would you predict this combustion reaction product- or reactant favored? ________________________________

(d) What is the change in entropy for the combustion reaction reaction?

i  \( \Delta S^\circ = -197 \text{ J/K}\cdot\text{mol} \)

ii \( \Delta S^\circ = -94.0 \text{ J/K}\cdot\text{mol} \)

iii \( \Delta S^\circ = +257 \text{ J/K}\cdot\text{mol} \)

iv \( \Delta S^\circ = +402 \text{ J/K}\cdot\text{mol} \)

5. (3 points) Rank the molecules below in terms of increasing strength of intermolecular forces in the pure substances:

(a) H₂  (b) H₃C—OH  (c) CO₂  (d) SO₂

________________________  __________________________  __________________________  __________________________

weakest force  strongest force
6. (4 points) Carbonates are not generally very soluble in water. Considering calcium and magnesium carbonates, which is the more soluble in water? ___________________

\[ \text{CaCO}_3(s) \rightleftharpoons \text{Ca}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_{sp} = 3.8 \times 10^{-9} \]

\[ \text{MgCO}_3(s) \rightleftharpoons \text{Mg}^{2+}(aq) + \text{CO}_3^{2-}(aq) \quad K_{sp} = 4.0 \times 10^{-5} \]

Assume you place some MgCO\(_3\) in a beaker containing 1.0 L of water. What mass of the solid dissolves? (Molar mass of MgCO\(_3\) = 84.31 g/mol)

(a) 0.0843 g
(b) 0.533 g
(c) 0.267 g
(d) 1.07 g

7. (5 points) The carbonate ion in water is a Brønsted _______________ because it can interact with water as follows:

\[ \text{CO}_3^{2-}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{HCO}_3^{-}(aq) + \text{OH}^{-}(aq) \]

What is the equilibrium constant for this reaction? _______________

If you have a 0.15 M solution of Na\(_2\)CO\(_3\), what are the concentrations of H\(_3\)O\(^+\) and OH\(^-\) and what is the pH of the solution?

<table>
<thead>
<tr>
<th>[H(_3)O(^+)]</th>
<th>[OH(^-)]</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 5.61 \times 10^{-3}</td>
<td>1.78 \times 10^{-12}</td>
<td>5.61</td>
</tr>
<tr>
<td>(b) 1.78 \times 10^{-12}</td>
<td>5.61 \times 10^{-3}</td>
<td>11.75</td>
</tr>
<tr>
<td>(c) 5.61 \times 10^{-3}</td>
<td>1.78 \times 10^{-12}</td>
<td>11.75</td>
</tr>
<tr>
<td>(d) 1.78 \times 10^{-12}</td>
<td>5.61 \times 10^{-3}</td>
<td>5.61</td>
</tr>
</tbody>
</table>

8. (3 points) The pH of a solution made by dissolving 0.588 g of the weak organic acid phenol (M = 94.114 g/mol) in 500. mL of water is 5.90. What is the value of K\(_a\) for the acid?

\[ \text{C}_6\text{H}_5\text{OH}(aq) + \text{H}_2\text{O}(\ell) \rightleftharpoons \text{C}_6\text{H}_5\text{O}^{-}(aq) + \text{H}_3\text{O}^+(aq) \]

(a) 5.0 \times 10^{-15}
(b) 2.5 \times 10^{-10}
(c) 1.0 \times 10^{-4}
(d) 1.3 \times 10^{-10}
9. (7 points) Nitrosyl bromide, NOBr(g), decomposes according to the equation

\[
\text{NOCl}(g) \rightleftharpoons \text{NO}(g) + \frac{1}{2} \text{Cl}_2(g)
\]

What is the free energy change, \(\Delta G^\circ\), for this reaction?

(a) -66.08 kJ
(b) -20.47 kJ
(c) +20.47 kJ
(d) +66.08 kJ
(e) +86.55 kJ

Is the reaction product- or reactant favored? ___________________________

Is the entropy change of the reaction predicted to be positive or negative? _________________

The reaction has an equilibrium constant of \(K_p = 2.6 \times 10^{-4}\) at 25 °C. If 2.0 atm of NOCl, 0.80 atm of NO, and 0.40 atm of Cl\(_2\) are mixed at 350 °C, is the reaction at equilibrium? ___________

If a net reaction is observed, will NOCl be formed or consumed? _______________

10. (3 points) The oxidation of NO to NO\(_2\), which occurs in the atmosphere, is \textit{exothermic}.

\[
2 \text{NO}(g) + \text{O}_2(g) \rightleftharpoons 2 \text{NO}_2(g)
\]

Predict the effect of the following changes on the position of the equilibrium; that is, state which way the equilibrium will shift (left, right, or no change) when each of the following changes is made.

(a) Add more \text{O}_2(g). ______________________
(b) Add more \text{NO}_2(g). ______________________
(c) Lower the temperature. ______________________

11. (6 points) For each solution below, tell if the pH is less than 7, equal to 7, or greater than 7.

<table>
<thead>
<tr>
<th>SOLUTION</th>
<th>pH (&gt;7, &lt;7, &gt;7)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(a) 0.10 M H(_2)SO(_4)</td>
<td>________</td>
</tr>
<tr>
<td>(b) 0.012 M KOH</td>
<td>________</td>
</tr>
<tr>
<td>(c) 0.15 M formic acid</td>
<td>________</td>
</tr>
<tr>
<td>(e) 0.45 M KBr</td>
<td>________</td>
</tr>
<tr>
<td>(f) 0.25 M Na(_3)PO(_4)</td>
<td>________</td>
</tr>
<tr>
<td>(i) 0.095 M FeCl(_3)</td>
<td>________</td>
</tr>
</tbody>
</table>
12. (3 points) What is the pH of the buffer solution that consists of 12.6 g of ammonium chloride dissolved in 150 mL of 1.8 M ammonia? (Molar mass for NH₄Cl = 53.49 g/mol and for NH₃ = 17.03 g/mol)

(a) 4.69
(b) 4.94
(c) 9.06
(d) 9.31
(e) 10.14

13. (4 points) Consider the reactions below. In each case you mix the acid and base so that they exactly react with one another; none of the original acid or base remains unreacted in solution. What is the pH of the solution after the acid-base reaction has occurred?

Reactions | pH ( = 7, < 7, > 7 )
--- | ---
KOH(aq) + HCl(aq) → products | _________
HC₂H₃O₂(aq) + NaOH(aq) → products | _________

GASES

14. (3 points) A bicycle tire that holds 0.406 mol of air, and which has a volume of 1.52 L, will burst if the pressure reaches 7.25 atm. What must the temperature be in order to burst the tire?

(a) 30 °C
(b) 37 °C
(c) 58 °C
(d) 100 °C

15. (3 points) A 250. mL flask holds 0.0156 g of an unknown gas collected from a pollutant source. The pressure of the gas is 38.3 mm Hg and the temperature is 22 °C. The unknown compound is

(a) CH₄
(b) N₂O
(c) CH₂O
(d) SO₂

16. (3 points) Air contains O₂, N₂, H₂O, and CO₂. Place these gas molecules in order of increasing average molecular velocity at 25 °C.

slowest molecule __________ __________ __________ __________ fastest molecule
LIQUIDS
17. (14 points) Properties of Liquids Use the vapor pressure curve to answer the questions below.

(a) What is the equilibrium vapor pressure of water at 80 °C? _______
(b) What is the temperature at which the equilibrium vapor pressure of water is 600 mm Hg? ________________
(c) Sketch the vapor pressure curve for methanol, CH₃OH, on the graph above using the data below. Mark the points given here on your plot.

- Vapor pressure at 30 °C = 161 mm Hg
- Vapor pressure at 50 °C = 411 mm Hg
- Normal boiling point = 64.6 °C.
(d) Based on comparison of their vapor pressures at comparable temperatures, which has the weaker intermolecular forces, H₂O or methyl alcohol? ____________
(e) If T = 70 °C and P = 500 mm Hg, is water a liquid, a vapor, or are both phases present in equilibrium? ________________________________
(f) Sketch a molecular drawing showing how water and methanol, CH₃OH, can interact via intermolecular forces.
KINETICS

18. (4 points) A reaction between molecules A and B (A + B → products) is found to be second order in A and first order in B. Which rate law below is correct?

(a) Rate = k\([A][B]\)  
(b) Rate = k\([A]^2[B]\)  
(c) Rate = k\([A][B]^2\)  
(d) Rate = k\([B]^2\)

When the concentration of A is doubled the rate of the reaction

(a) doubles  
(b) goes up by a factor of four  
(c) is cut in half  
(d) does not change

19. (3 points) The following reaction between methyl alcohol and an organic halide occurs in benzene at 25 °C (when a weak base is present).

\[
\text{CH}_3\text{OH} + (\text{C}_6\text{H}_5)_3\text{C-Cl} \rightarrow (\text{C}_6\text{H}_5)_3\text{C-OCH}_3 + \text{HCl}
\]

In order to study its mechanism, the following data were collected:

<table>
<thead>
<tr>
<th>Initial Concentrations</th>
<th>Initial Rate of Appearance of C</th>
</tr>
</thead>
<tbody>
<tr>
<td>[A]</td>
<td>[B]</td>
</tr>
<tr>
<td>0.10</td>
<td>0.05</td>
</tr>
<tr>
<td>0.10</td>
<td>0.10</td>
</tr>
<tr>
<td>0.20</td>
<td>0.10</td>
</tr>
</tbody>
</table>

The rate law for the process is

(a) Rate = k\([A]^2[B]^2\)  
(b) Rate = k\([A]^2[B]\)  
(c) Rate = k\([A][B]^2\)  
(d) Rate = k\([A][B]\)  
(e) Rate = k\([A]^2\)  
(f) Rate = k\([B]^2\)

20. (3 points) Gas Laws and Kinetics

Hypofluorous acid, HOF, decomposes to HF and O₂ in a reaction that is first order in HOF and that has a half-life of 30.0 minutes.

\[
\text{HOF}(g) \rightarrow \text{HF}(g) + \frac{1}{2}\text{O}_2(g)
\]

Assume the partial pressure of HOF in a 1.0-L flask at 25 °C is initially 200. mm Hg. What is the TOTAL pressure in the flask after 1.5 hours (90 minutes)?

(a) 100. mm Hg  
(b) 275 mm Hg  
(c) 250. mm Hg  
(d) 287.5 mm Hg
21. (3 points) The plasma half-life of aspirin is 15 minutes. If you take a tablet containing 200 mg of aspirin, how much remains after 1.0 hour?
(a) 200 mg
(b) 100 mg
(c) 50 mg
(d) 25 mg
(e) 12.5 mg

ELECTROCHEMISTRY

22. (8 points) Use the small table of reduction potentials below to answer the electrochemistry questions that follow.

<table>
<thead>
<tr>
<th>Half Reaction</th>
<th>( E^o ) (volts)</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{Cl}_2(g) + 2e^- \rightarrow 2 \text{Cl}^-(aq) )</td>
<td>+1.36</td>
</tr>
<tr>
<td>( \text{Ag}^+(aq) + e^- \rightarrow \text{Ag(s)} )</td>
<td>+0.80</td>
</tr>
<tr>
<td>( \text{I}_2(s) + 2e^- \rightarrow 2 \text{I}^-(aq) )</td>
<td>+0.535</td>
</tr>
<tr>
<td>( \text{Cu}^{2+}(aq) + 2e^- \rightarrow \text{Cu(s)} )</td>
<td>+0.34</td>
</tr>
<tr>
<td>( \text{Pb}^{2+}(aq) + 2e^- \rightarrow \text{Pb(s)} )</td>
<td>-0.126</td>
</tr>
<tr>
<td>( \text{Ni}^{2+}(aq) + 2e^- \rightarrow \text{Ni(s)} )</td>
<td>-0.25</td>
</tr>
<tr>
<td>( \text{Zn}^{2+}(aq) + 2e^- \rightarrow \text{Zn(s)} )</td>
<td>-0.76</td>
</tr>
<tr>
<td>( \text{V}^{2+}(aq) + 2e^- \rightarrow \text{V(s)} )</td>
<td>-1.18</td>
</tr>
<tr>
<td>( \text{Al}^{3+}(aq) + 3e^- \rightarrow \text{Al(s)} )</td>
<td>-1.66</td>
</tr>
</tbody>
</table>

(a) What is the weakest oxidizing agent in the list above?  __________
(b) What is the strongest oxidizing agent above?  ___________
(c) What is the strongest reducing agent?  __________
(d) What is the weakest reducing agent?  __________
(e) Will \( \text{Pb(s)} \) reduce \( \text{V}^{2+}(aq) \) to \( \text{V(s)} \)?  __________
(f) Will \( \text{Cl}_2(g) \) oxidize \( \text{I}^-(aq) \) to \( \text{I}_2(s) \)?  __________
(g) Name or give symbols for the ions or compounds that can be reduced by \( \text{Pb(s)} \)  __________

(g) If you construct a battery from \( \text{I}_2 \) and \( \text{I}^- \) and \( \text{Zn} \) and \( \text{Zn}^{2+} \) half-cells, what will be the cell potential, \( E^\text{cell}_e \)?  __________________________________ V
23. (11 points) Consider the crude battery diagrammed below.

(a) The reaction that occurs spontaneously when the Hg\(^{2+}\) and Zn\(^{2+}\) ions have a concentration of 1 M is
   (i) \(\text{Hg}(l) + \text{Zn}^{2+}(aq) \rightarrow \text{Hg}^{2+}(aq) + \text{Zn}(s)\)
   (ii) \(\text{Zn}(s) + \text{Hg}^{2+}(aq) \rightarrow \text{Zn}^{2+}(aq) + \text{Hg}(l)\)

(b) The voltage observed on the voltmeter is \(E_{\text{cell}} = \) \underline{\hspace{2cm}}. The polarity of the Zn strip (+ or –) is \underline{\hspace{1cm}}. The cathode of the cell is \underline{\hspace{5cm}}. The direction of the electron flow in the external wire is (from Hg to Zn)(from Zn to Hg) \underline{\hspace{5cm}}

(c) The salt bridge contains NaNO\(_3\). The NO\(_3^-\) ions flow
   (i) from the Hg\(^{2+}\) beaker to the Zn\(^{2+}\) beaker
   (ii) from the Zn\(^{2+}\) beaker to the Hg\(^{2+}\) beaker

(d) If the cell passes 0.036 amps of current for 6.0 hours, what mass of Zn is consumed or deposited at the electrode? (Show you work!)
24. (6 points) A reaction you performed in the laboratory is the oxidation of zinc with nitric acid. Write a balanced, net ionic equation for the reaction of zinc metal with NO₃⁻ ion in acid solution to give zinc(II) ion and NO.

(a) Balanced half-reaction involving Zn → Zn²⁺

(b) Balanced half reaction for NO₃⁻ → NO

(c) Balanced overall, net ionic equation

25. (3 points) Acid-base titrations.

(a) What is the pH at the equivalence point in the titration whose curve is given?

(b) Identify the titration curve as one of the following:
   i. a strong acid titrated with a strong base
   ii. a strong base titrated with a strong acid
   iii. a strong acid titrated with a weak base
   iv. a weak base titrated with a strong acid
   v. a weak acid titrated with a strong base
LAB QUESTION  (5 points)

In a laboratory experiment this semester, you were given a solution that could have contained any or all of the ions Al$^{3+}$, Fe$^{3+}$, Ni$^{2+}$, and Pb$^{2+}$. Your unknown had a faint green tint, and, on adding HCl(aq), you observed a white precipitate (A). The solution (B) was still light green.

The white precipitate (A) was separated from the solution (B). To test the white precipitate, you found it dissolved in warm water. Then, when K$_2$CrO$_4$was added, you observed a yellow precipitate.

The light green solution (B) was treated with NaOH(aq), and a greenish precipitate (C) was observed. A colorless solution (D) was separated from the precipitate.

Time to work in the lab had run out! You could only turn in your best guess as to the composition of your unknown.

Ion(s) probably present ________________

Ion(s) probably NOT present ________________

Ion(s) for which you have no clue ________________

Write a **balanced net ionic equation** for the reaction of Ni$^{2+}$(aq) with aqueous ammonia to give insoluble Ni(OH)$_2$. 
CORRECTION

PAGE 3

Question 11, part (d)

One of the correct answers is given below
Circle the corresponding letter on your exam.

(d) What is the change in entropy for the combustion reaction reaction?

i $\Delta S˚ = -19.7 \text{ J/K}\cdot\text{mol}$

ii $\Delta S˚ = -94.0 \text{ J/K}\cdot\text{mol}$

iii $\Delta S˚ = +357 \text{ J/K}\cdot\text{mol}$

iv $\Delta S˚ = +40.2 \text{ J/K}\cdot\text{mol}$