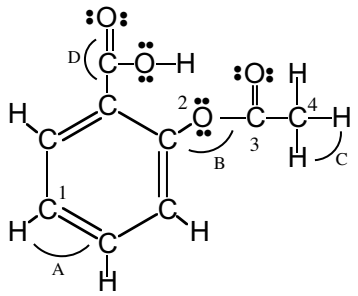
1. (16 points) Acetylsalicylic acid, the molecule pictured here, is better known as aspirin.



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 C_6 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) 2.45×10^{-3} M

(b) 2.61×10^{-4} M

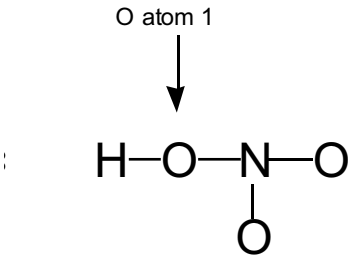
(c) 3.27×10^{-4} M

(d) 4.07×10^{-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.

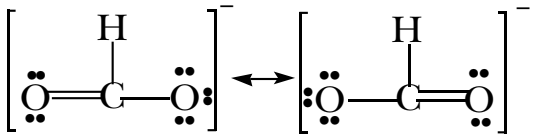


The formal charge on the central N is _____ and its hybridization is _____. The formal charge on the O atom marked 1 is _____ and its hybridization is _____. The O—N—O angle is about _____degrees, while the H—O—N is _____degrees.

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_2^-, is a common ion in natural systems.



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, $NaHCO_2$?

(a) 3.75

(b) 5.54

(c) 8.46

(d) 10.25

4. (11 points) The chemistry of sulfur dioxide, SO_2, and sulfur trioxide, SO_3.

(a) Draw an electron dot structure for SO_2 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 SO_2 can be liquefied at –75 ˚C. What intermolecular force is responsible for the attraction between SO_2 molecules? _____

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

$$SO_2(g) + 1/2\ O_2(g) \rightarrow SO_3(g)$$

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

_____

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

i $\Delta S^\circ = -197$ J/K•mol

ii $\Delta S^\circ = -94.0$ J/K•mol

iii $\Delta S^\circ = +257$ J/K•mol

iv $\Delta S^\circ = +402$ J/K•mol

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

(a) H_2 (b) H_3C—OH (c) CO_2 (d) SO_2

_____ _____ _____ _____

weakest force strongest force

CHEMICAL EQUILIBRIA

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

$CaCO_3(s) \rightleftharpoons Ca^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 3.8 \times 10^{-9}$

$MgCO_3(s) \rightleftharpoons Mg^{2+}(aq) + CO_3^{2-}(aq)$ $K_{sp} = 4.0 \times 10^{-5}$

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:

$$CO_3^{2-}(aq) + H_2O(\ell) \rightleftharpoons HCO_3^{-}(aq) + OH^{-}(aq)$$

What is the equilibrium constant for this reaction? _____

If you have a 0.15 M solution of Na_2CO_3, what are the concentrations of H_3O^+ and OH^- and what is the pH of the solution?

	$[H_3O^+]$	**$[OH^-]$**	**pH**
(a)	5.61×10^{-3}	1.78×10^{-12}	5.61
(b)	1.78×10^{-12}	5.61×10^{-3}	11.75
(c)	5.61×10^{-3}	1.78×10^{-12}	11.75
(d)	1.78×10^{-12}	5.61×10^{-3}	5.61

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?

$$C_6H_5OH(aq) + H_2O(\ell) \rightleftharpoons C_6H_5O^{-}(aq) + H_3O^{+}(aq)$$

(a) 5.0×10^{-15}

(b) 2.5×10^{-10}

(c) 1.0×10^{-4}

(d) 1.3×10^{-10}

9. (7 points) Nitrosyl bromide, NOBr(g), decomposes according to the equation

$$NOCl(g) \rightleftharpoons NO(g) + 1/2\ Cl_2(g)$$

What is the free energy change, ΔG°, 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 ***exothermic***.

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

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 $O_2(g)$. _____

(b) Add more $NO_2(g)$. _____

(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.

SOLUTION	pH (=7, <7, >7)
(a) 0.10 M H_2SO_4	_____
(b) 0.012 M KOH	_____
(c) 0.15 M formic acid	_____
(e) 0.45 M KBr	_____
(f) 0.25 M Na_3PO_4	_____
(i) 0.095 M $FeCl_3$	_____

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 NH_4Cl = 53.49 g/mol and for NH_3 = 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?

Reaction	**pH (=7, <7, >7)**
$KOH(aq) + HCl(aq) \rightarrow$ products	_____
$HC_2H_3O_2(aq) + NaOH(aq) \rightarrow$ 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) CH_4

    (b) N_2O

    (c) CH_2O

    (d) SO_2

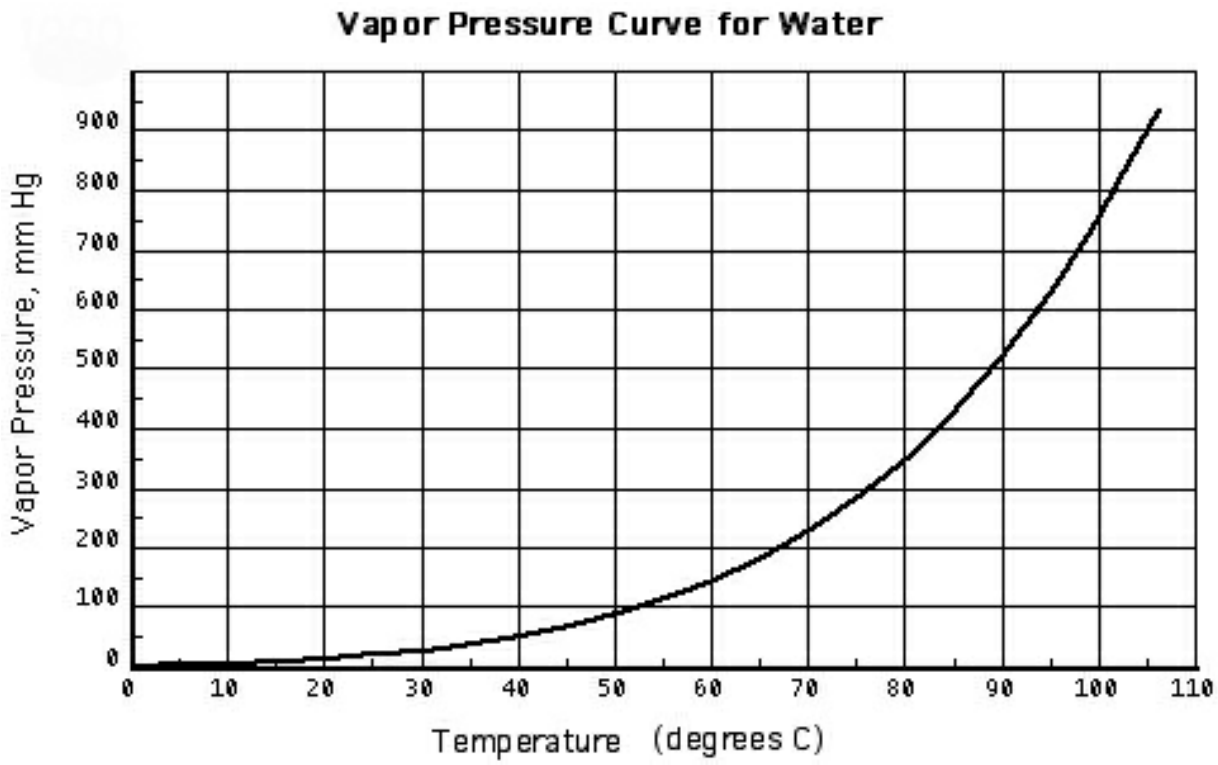
16. (3 points) Air contains O_2, N_2, H_2O, and CO_2. Place these gas molecules in order of increasing average molecular velocity at 25 ˚C.

_____ _____ _____ _____

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, CH_3OH, 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, H_2O 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, CH_3OH, 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] (c) Rate = k[A][B]^2

(b) Rate = k[A]^2[B] (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).

$$CH_3OH + (C_6H_5)_3C\text{-}Cl \rightarrow (C_6H_5)_3C\text{-}OCH_3 + HCl$$
$$\quad A \qquad\quad B \qquad\qquad C$$

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

Initial Concentrations		**Initial Rate of Appearance of C**
[A]	**[B]**	**mol/L-min**
0.10	0.05	1.32×10^{-4}
0.10	0.10	2.60×10^{-4}
0.20	0.10	10.3×10^{-4}

The rate law for the process is

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

(b) Rate = k[A]^2[B] (e) Rate = k[A]^2

(c) Rate = k[A][B]^2 (f) Rate = k[B]^2

20. (3 points) *Gas Laws and Kinetics*

Hypofluorous acid, HOF, decomposes to HF and O_2 in a reaction that is first order in HOF and that has a half-life of 30.0 minutes.

$$HOF(g) \rightarrow HF(g) + 1/2\ O_2(g)$$

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.

Half Reaction		***E° (volts)***
$Cl_2(g) + 2e^-$	$\rightarrow 2\ Cl^-(aq)$	+1.36
$Ag^+(aq) + e^-$	$\rightarrow Ag(s)$	+0.80
$I_2(s) + 2e^-$	$\rightarrow 2\ I^-(aq)$	+0.535
$Cu^{2+}(aq) + 2e^-$	$\rightarrow Cu(s)$	+0.34
$Pb^{2+}(aq) + 2e^-$	$\rightarrow Pb(s)$	-0.126
$Ni^{2+}(aq) + 2e^-$	$\rightarrow Ni(s)$	-0.25
$Zn^{2+}(aq) + 2e^-$	$\rightarrow Zn(s)$	-0.76
$V^{2+}(aq) + 2e^-$	$\rightarrow V(s)$	-1.18
$Al^{3+}(aq) + 3e^-$	$\rightarrow Al(s)$	-1.66

(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? _____

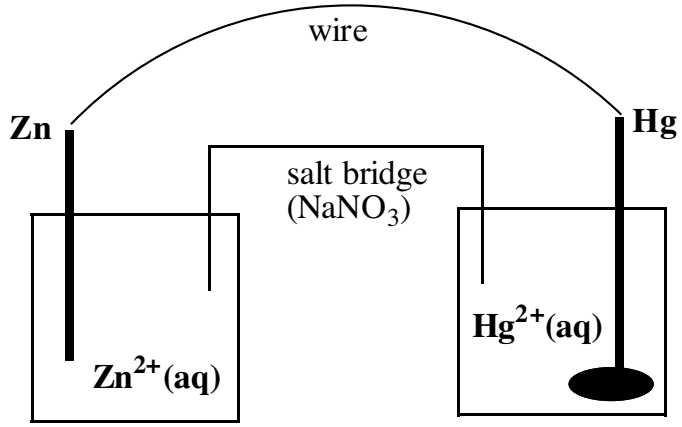
(e) Will Pb(s) reduce $V^{2+}(aq)$ to V(s)? _____

(f) Will $Cl_2(g)$ oxidize $I^-(aq)$ to $I_2(s)$? _____

(g) Name or give symbols for the ions or compounds that can be reduced by Pb(s) _____

(g) If you construct a battery from I_2 and I^- and Zn and Zn^{2+} half-cells, what will be the cell potential, E°_{cell}? _____ 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) $Hg(\ell) + Zn^{2+}(aq) \rightarrow Hg^{2+}(aq) + Zn(s)$

(ii) $Zn(s) + Hg^{2+}(aq) \rightarrow Zn^{2+}(aq) + Hg(\ell)$

(b) The voltage observed on the voltmeter is E°_{cell} = _____. The polarity of the Zn strip (+ or –) is _____. The cathode of the cell is _____. The direction of the electron flow in the external wire is *(from Hg to Zn)(from Zn to Hg)* _____

(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 perrformed in the laboratory is the oxidation of zinc with nitric acid. Write a balanced, net ionic equation for the reaction of zinc metal with NO_3^- ion in acid solution to give zinc(II) ion and NO.

(a) Balanced half-reaction involving $Zn \rightarrow Zn^{2+}$

(b) Balanced half reaction for $NO_3^- \rightarrow NO$

(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:

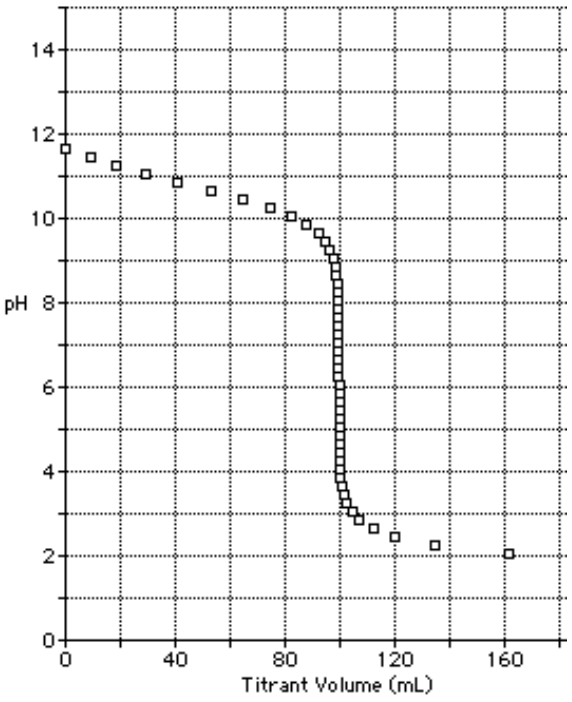
i. a strong acid titrated with a strong base

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_2CrO_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 in given below
Circle the corresponding letter on your exam.

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

i $\Delta S^\circ = -19.7\ J/K\bullet mol$

ii $\Delta S^\circ = -94.0\ J/K\bullet mol$

iii $\Delta S^\circ = +357\ J/K\bullet mol$

iv $\Delta S^\circ = +40.2\ J/K\bullet mol$