

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A Midterm #1 A Fall 2013

Please keep your work covered at all times and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the university.

There are 10 pages in this test. A periodic table and data sheets are provided at the end. You may rip these pages off of the exam and use them to cover your work during the test. Any scratch work should be done on the back of these pages.

Please show all work to receive partial credit.

You have 80 minutes to complete the test.

#1. (10 points) Short Answer Questions

a) Provide the name or formula for the following:

magnesium sulphate pentahydrate _____

 $\text{Fe}(\text{BrO}_4)_3$ _____

b) Four balloons are filled to the same volume with the following gases. If a small hole is made in each balloon, which will deflate the fastest?

 SO_3 H_2S N_2 CO_2

c) The enthalpy of vaporization of sodium is 96.96 kJ/mol at 1156 K. The amount of heat (in kJ) needed to vaporize 1.00 g of sodium is: _____.

d) A sample of a gas is slowly compressed from 8.0 L to 4.0 L. In order for the internal energy of the gas to remain constant, the gas must also be simultaneously cooled.

TRUE FALSE

e) Give the full, precise chemical symbol for the following:

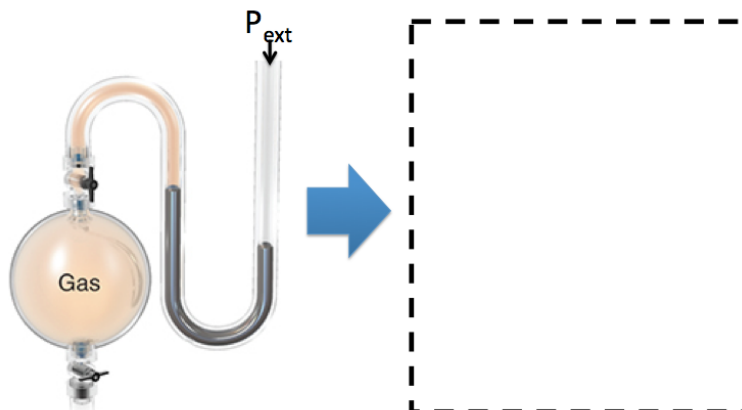
Number of protons	Number of neutrons	Number of electrons	Chemical Symbol
17	20	18	

f) The standard heat of formation of solid sodium bicarbonate is -654 kJ. Write the chemical equation for the reaction to which this value applies (include phases).

g) Two sets of successive reactions, $A \rightarrow B$ and $B \rightarrow C$, have respective percent yields of 48% and 73%. The overall percent yield for the conversion of A to C is: _____.h) Rank the following compounds in *increasing* order of oxidation state of iodine:NaOI, HI, I_2 _____

BONUS:

The figure on the left shows 1 mol of gas in an open-end manometer. The external pressure is 1.0 bar and the temperature is 300K. In the box, sketch the manometer and qualitatively show the effect on the gas if the external pressure increases to 2.0 bar and the temperature is increased to 600K.



#2. (10 points) 15.0 kg of ammonium nitrate decomposes to nitrogen, oxygen, and water vapour.

a) What is the total volume of gas (in L) that will form at 307°C and 1.01 bar?

Answer: _____

b) What is the partial pressure of nitrogen in the product mixture?

Answer: _____

#3. (10 points) A calorimeter contains 24.0 mL of water at 13.0°C. When 2.20 g of X (molar mass 47.0 g/mol) is added, it dissolves via the reaction: $X(s) \rightarrow X(aq)$ and the temperature of the solution increases to 28.0°C.

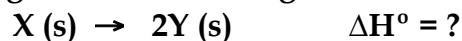
- a) Calculate the enthalpy change for the dissolution, in kJ/mol. You may assume the specific heat capacity and density of the solution are equal to those of pure water; however, you may NOT assume that the mass of the solution is equal to the mass of the water.

Answer: _____

- b) Calculate the internal energy change for the dissolution, in kJ/mol.

Answer: _____

- c) Determine the enthalpy change for the following reaction, using the provided data.



$Y(s) \rightarrow Y(aq)$	$\Delta H^\circ = +24.7 \text{ kJ}$
$2 Y(aq) \rightarrow X(aq)$	$\Delta H^\circ = -1.44 \text{ kJ}$

Answer: _____

#4. (10 points) Dr. Fox's favourite single malt scotch whisky is *Lagavulin*, which is 43% ethanol (C_2H_5OH) by volume. While marking midterms, Dr. Fox drinks 30 mL of the scotch, of which 22% of the ethanol by mass is absorbed into her blood.

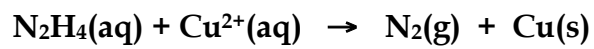
- a) If Dr. Fox has 6.5 L of blood, what concentration (in g/mL) of ethanol is in her blood? (*d* of ethanol = 0.789 g/mL)

Answer: _____

- b) What volume (mL) of scotch would raise Dr. Fox's blood alcohol level to 8.0×10^{-4} g/mL, the level at which she would be considered intoxicated and no longer able to mark midterms?

Answer: _____

#5. (10 points) The following reaction is one route to solid copper metal.



a) Determine the overall balanced redox equation in basic solution.

b) Label the oxidizing agent and reducing agent.

c) 1.54 g of N_2H_4 (MM = 32.05 g/mol) are added to 50.0 mL of a 1.55 M copper (II) hydroxide solution. What is the volume of nitrogen gas produced, at 1.01 bar and 20.0°C?

Answer: _____

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A Midterm #2 A Fall 2013

Please keep your work covered at all times and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the university.

There are 10 pages in this test. A periodic table, data tables, and a formula sheet are provided at the end. You may gently remove these pages off and use them to cover your work. Any scratch work should be done on the back of these pages.

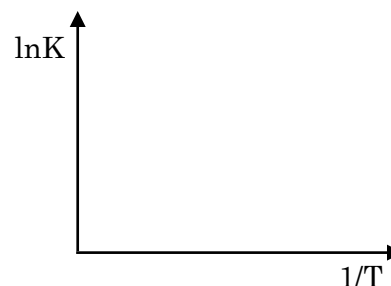
Please show all work to receive partial credit.

You have 80 minutes to complete the test.

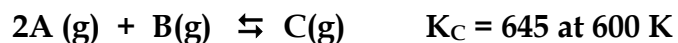
Question	Points Possible	Points Earned	TA Initial
1	20		
2	10		
3	10		
4	10		
5	10		
TOTAL	50		

1. (10 points) Short Answer Questions

- a. On the axes provided at right, draw the expected line (or curve) of a van't Hoff plot for an exothermic reaction.



- b. Exactly 2.00 mol of A, 2.00 mol of B, and 2.00 mol of C are placed in a sealed 1.00 L flask at 600K.



The reaction will proceed towards (circle one) REACTANTS PRODUCTS
because _____.

- c. The equivalence point of a titration is the point at which the indicator changes colour.

TRUE

FALSE

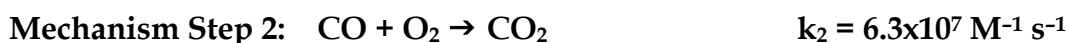
- d. If the equilibrium constant for the reaction $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ is K_a , then the equilibrium constant for the reaction $H_3O^+ + A^- \rightleftharpoons HA + H_2O$ would be

K_a K_w/K_a $1/K_a$ K_b

- e. For the majority of reactions, reaction rate is fastest when:

E_a high, T low E_a high, T high E_a low, T low E_a low, T high

- f. From the given mechanism, what is the overall reaction and its expected rate law?



Overall Reaction: _____ rate = _____

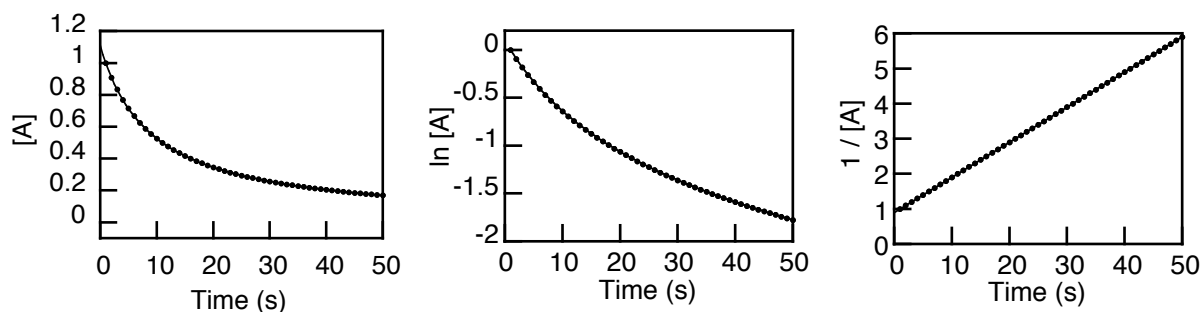
- g. A buffer solution is prepared from 0.450 M HCN and 0.450 M NaCN. The pH of this solution is _____.

BONUS:

Classify the following as either Brønsted or Arrhenius bases.

NH ₃	Brønsted	Arrhenius
NaOH		
PO ₄ ³⁻		

2. The progress of the reaction below is followed for 50 seconds at 298 K.



a). (1 pt) What is the order of the reaction? _____

b). (3 pts) What is the rate constant for this reaction at this temperature?

Answer: _____

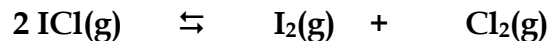
c). (3 points) What is the half-life of this reaction?

Answer: _____

d). (3 pts) What will [A] be after 30 seconds if its initial concentration is 0.755 M?

Answer: _____

3. In an analysis of interhalogen reactivity, 0.500 mol of ICl was placed in a 5.00 L flask, where it decomposed at 800K:



- a) (5 points) What are the equilibrium concentrations of each species? $K_C = 0.110$ at 800K

[ICl] = _____ [I₂] = _____ [Cl₂] = _____

- b) (5 points) Using the data above and below, find the value of K_P for the indicated reaction.

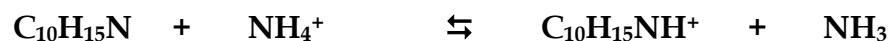
Reaction	K_P
$\text{HCl(g)} \rightleftharpoons \frac{1}{2} \text{H}_2\text{(g)} + \frac{1}{2} \text{Cl}_2\text{(g)}$	2.54
$2 \text{ICl(g)} + \text{H}_2\text{(g)} \rightleftharpoons \text{I}_2\text{(g)} + 2\text{HCl(g)}$?

Answer: _____

4. A certain New Mexico chemistry teacher (let's call him "Heisenberg") decides to supplement his income by synthesizing and selling methamphetamine, $C_{10}H_{15}N$ (MM = 149.2 g/mol). To ship it undetected, he disguises it by creating aqueous solutions (meth has an aqueous solubility of 0.011 g/100 mL).

a) A saturated solution of this compound has a pH = 10.08. What is the value of K_b ?

b) Ammonia, NH_3 , has a K_b of 1.8×10^{-5} . On the equilibrium below, label the acid, base, conjugate acid and conjugate base, and predict the preferred direction of the reaction (i.e. towards reactants or products?). To obtain full marks, show your reasoning.



6. Your TA informs you that you will be performing a titration of 25.00 mL of 0.100 M acetic acid with 0.100 M NaOH.
- a) (3 pts) What is the initial pH (before any NaOH is added)?

Answer: _____

- b) (3 pts) What is the pH at the half-equivalence point?

Answer: _____

- c) (4 pts) Which of the following indicators is an appropriate choice for this titration? Show your calculations or explain your reasoning to obtain full marks.

Indicator	pH Range
Thymol Blue	8 to 10
Bromocresol Green	4 to 6
Methyl Violet	0 to 2

Answer: _____

Surname (last name): _____

Given name (First name): _____

Student Number: _____

Seat Number: _____

CHM 1311 A Final Exam December 2013

Attention: If you didn't have Dr. Focsaneanu (Fox) as your Instructor, you shouldn't be writing this exam!

Please keep your work covered at all times and keep your eyes on your own paper! Cheating or any appearance of cheating will result in an F in the course and possible expulsion from the university.

There are 15 pages in this test. A periodic table, data tables, and a formula sheet are provided at the end. You may gently remove these pages from the exam and use them to cover your work. Any scratch work should be done on the back of these pages.

Please show all work to receive partial credit.

You have 180 minutes to complete the exam.

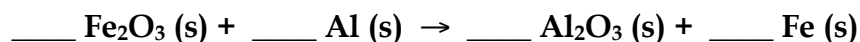
1. (20 points) Short Answer Questions.

a) Give the name or formula for the following compounds:

Tin (II) oxide _____

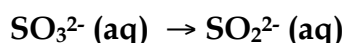
Sulfurous acid _____

b) Balance the following reaction:



When 50.00 g of iron (III) oxide was reacted with excess aluminum, 28.65 g of solid iron was formed. The percent yield of the reaction is _____.

c) Determine if the following half-reaction (in acidic solution) is an oxidation or a reduction and the number of electrons gained/lost in the process.



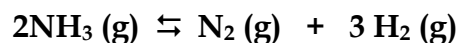
OXIDATION REDUCTION # of electrons = _____

d) The standard heat of formation of *one mole* of solid sodium carbonate is -1 131 kJ. Write the chemical equation for the reaction to which this value applies.

e) Under constant pressure conditions, the heat absorbed/released by a chemical reaction is equal to:

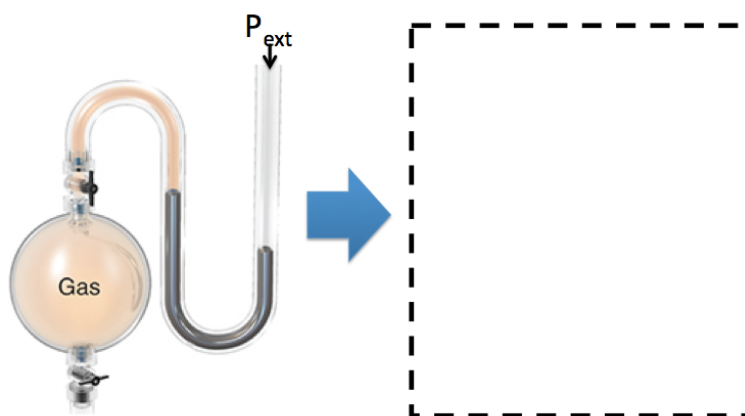
$$\Delta U \qquad \Delta H \qquad 0 \qquad q_v \qquad w$$

f) For the following reaction

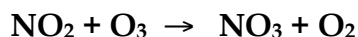


the value of K_c is 2.8×10^{-9} at 298 K. Therefore, K_p for this reaction is _____.

g) The figure on the left shows 1 mol of gas in an open-end manometer. The external pressure is 1.0 bar and the temperature is 300K. In the box, sketch the manometer and qualitatively show the effect on the gas if the external pressure increases to 2.0 bar and the temperature is increased to 600K.



- h) Determine the rate law and value of k for the following reaction using the data provided.



$[\text{NO}_2]_i$ (M)	$[\text{O}_3]_i$ (M)	Initial rate (M/s)
0.10	0.33	1.42
0.10	0.66	2.84
0.25	0.66	7.10

Rate Law = _____

Value of k : _____

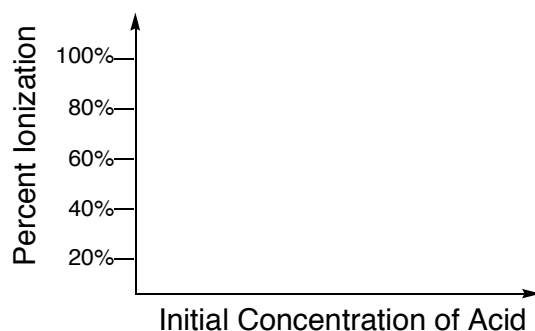
- i) Name two factors that influence the speed of a chemical reaction:

i. _____

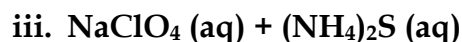
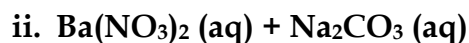
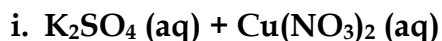
ii. _____

- j) The conjugate acid and conjugate base of H_2PO_4^- are _____ and _____, respectively.

- k) On the axes provided below, draw a line (or curve) representing the percent ionization of a weak acid as a function of the initial concentration of the acid.



- l) The mixing of one of these pairs of reactants will result in a precipitation reaction. Indicate the correct pair and give the formula of the expected precipitate.



Precipitate: _____

- m) The maximum number of electrons that can have the designation $3p$ is _____.

- n) Cesium's outermost electron is in an orbital with quantum numbers $n = 6$, $\ell = 0$, $m_\ell = 1$.

TRUE

FALSE

2. You are given 200.0 mL of an aqueous solution that contains 0.250 M each of Ag^+ , Pb^{2+} and Ba^{2+} . You wish to precipitate these cations sequentially by adding chromate to the solution.
- a) (4 points) In what order will the solids precipitate as chromate is added to the above solution?

First = _____ Second = _____ Third = _____

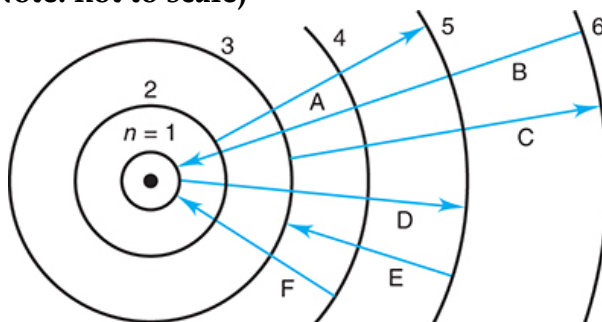
- b) (2 points) What concentration of chromate will cause the first precipitation?

Answer: _____

- c) (4 points) At the point *just before* BaCrO_4 begins to precipitate, what will be the concentration of all of the ions in solution?

$[\text{Ag}^+] =$ _____ $[\text{Pb}^{2+}] =$ _____ $[\text{Ba}^{2+}] =$ _____

3. A Bohr-model representation of the H atom is shown below, with several transitions depicted by arrows. (Note: not to scale)



- a) (2 points) Which transitions are absorptions, and which are emissions?
- b) (3 points) Rank the absorptions in terms of increasing energy.
- c) (3 points) Rank the emissions in terms of increasing wavelength of light emitted.
- d) (2 points) This model does not work for any element other than hydrogen. Briefly explain why.

4. You wish to prepare a 100 mL solution that is 0.0100 M MgCl_2 and also 0.100 M NH_3 . You have access to solid MgCl_2 and a concentrated stock solution of 2.88 M NH_3 .
- a) (4 points) Determine the mass of MgCl_2 and the volume of NH_3 you need to prepare your solution.

mass of MgCl_2 = _____ volume of NH_3 = _____

- b) (2 points) Your lab TA warns you that, when preparing solutions of Mg^{2+} (aq) and NH_3 (aq), a precipitate of $\text{Mg}(\text{OH})_2$ (s) may form, depending on the concentrations. Write the chemical equation and the K_{sp} expression for the formation of this precipitate.
- c) (4 points) Considering the solution prepared in part (a), will you observe a precipitate? The K_{b} for ammonia is 1.8×10^{-5} . Please show your work.

Answer (circle one):

YES

NO

5. The total amount of sulfur released into the atmosphere per year by the burning of coal is about 75 million metric tonnes (1000 kg = 1 t).
- a) (5 points) Assuming this were all solid sulfur, how big a cube would this occupy? Find the dimension of each side of the cube in metres. The density of sulfur is 2.0 g/cm^3 .

Answer: _____

- b) (5 points) A rare but stable isotope of sulfur is sulfur-33, with a percent natural abundance of only 0.75%. How many atoms of sulfur-33 would be present in the cube of part (a)?

Answer: _____

6. Methanol, CH_3OH , is synthesized directly on the industrial scale by the reaction of carbon monoxide with hydrogen gas.

a) (1 point) Write a balanced chemical equation for this reaction.

b) (3 points) Using the data below, what is the value for the enthalpy change of the reaction of part (a) at 25°C ?

	ΔH_f° (kJ/mol)
CO(g)	-110.5
$\text{CO}_2\text{(g)}$	-393.5
$\text{H}_2\text{(g)}$	0.0
$\text{H}_2\text{O(g)}$	-241.8
$\text{CH}_3\text{OH(g)}$	-200.7
$\text{CH}_4\text{(g)}$	-74.87

Answer: _____

c) (4 points) The value of the equilibrium constant for the above reaction at 298 K is 2.27×10^4 . Calculate the value of the equilibrium constant at 500 K.

Answer: _____

d) (2 points) Based on your answer in part (c), what effect does changing the temperature from 298 K to 500 K have on the equilibrium?

7. When Dr. Fox goes scuba diving, she uses NITROX, a special blend of enriched air that allows for more repetitive dives by reducing the build-up of nitrogen in the blood (that way, she won't get "the bends"!). The local scuba shop prepares 5.00 L tanks of NITROX by mixing 26.0 g of O₂ with 44.2 g of N₂ at a temperature of 25.0°C.

a) What is the mole fraction of each gas in the mixture?

$$\chi \text{ of N}_2 = \underline{\hspace{2cm}} \qquad \chi \text{ of O}_2 = \underline{\hspace{2cm}}$$

b) What is the partial pressure of each gas, in atm?

$$P \text{ of N}_2 = \underline{\hspace{2cm}} \qquad P \text{ of O}_2 = \underline{\hspace{2cm}}$$

c) What will be the total pressure left in the tank after Dr. Fox breathes 80% of it by volume during a dive?

$$P_T = \underline{\hspace{2cm}}$$

8. You are asked to prepare a buffer solution with a pH of 5.00. Exactly 500 mL of each of the following solutions, all 0.100 M, are available to you: formic acid, acetic acid, sodium formate and sodium acetate.

a) (3 points) Which solutions would you use to prepare this buffer, and what would be the required base-to-acid ratio for a pH of 5.00?

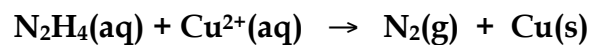
b) (3 points) As mentioned, you only have 500 mL of each 0.100 M solution. You are asked to make as much buffer as possible from the available solutions (i.e. the maximum volume possible). What would be the final total volume of the buffer? You may assume that volumes are additive.

Answer: _____

c) (4 points) If 0.965 mL of 8.00 M Ba(OH)₂ is added to the buffer, prepared in part (b), what will be the new pH?

Answer: _____

9. The following reaction is one route to solid copper metal.



- a) (4 points) Determine the overall balanced redox equation in basic solution.
- b) (2 points) Label the oxidizing agent and reducing agent.
- c) (4 points) 1.54 g of N_2H_4 (MM = 32.05 g/mol) are added to 50.0 mL of a 1.55 M copper (II) hydroxide solution. What is the volume of nitrogen gas produced, at 1.01 bar and 20.0°C?

Answer: _____

#1. (10 points) Short Answer Questions

a) Provide the name or formula for the following:

magnesium sulphate pentahydrate $MgSO_4 \cdot 5H_2O$ $Fe(BrO_4)_3$ iron (III) perbromate or ferric perbromate

b) Four balloons are filled to the same volume with the following gases. If a small hole is made in each balloon, which will deflate the fastest?

According to Graham's Law, the lightest gas = fastest effusion. Therefore: SO_3 H_2S N_2 CO_2

c) The enthalpy of vaporization of sodium is 96.96 kJ/mol at 1156 K.

The amount of heat (in kJ) needed to vaporize 1.00 g of sodium is: _____.

$$? \text{ kJ} = 1.00 \text{ g Na} \times \frac{\text{mol Na}}{22.99 \text{ g}} \times \frac{96.96 \text{ kJ}}{\text{mol Na}} = + 4.22 \text{ kJ}$$

d) A sample of a gas is slowly compressed from 8.0 L to 4.0 L. In order for the internal energy of the gas to remain constant, the gas must also be simultaneously cooled.

$$\Delta U = q + W$$

If the internal energy is constant, then $\Delta U = 0$ (no change).**Compression of a gas means that W is positive. Therefore, to keep $\Delta U = 0$, q must be negative. In other words, heat must be emitted from the system (it must cool down).****TRUE FALSE**

e) Give the full, precise chemical symbol for the following:

Number of protons	Number of neutrons	Number of electrons	Chemical Symbol
17	20	18	${}^{37}_{17}Cl^-$

f) The standard heat of formation of solid sodium bicarbonate is -654 kJ. Write the chemical equation for the reaction to which this value applies (include phases).

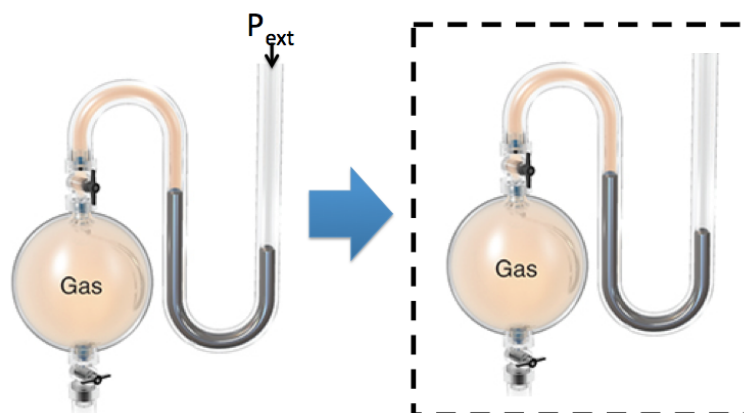
g) Two sets of successive reactions, $A \rightarrow B$ and $B \rightarrow C$, have respective percent yields of 48% and 73%. The overall percent yield for the conversion of A to C is: 35%.h) Rank the following compounds in *increasing* order of oxidation state of iodine:

NaOI, HI, I_2 HI, I_2 , NaOI

+1 -1 0

BONUS:

The figure on the left shows 1 mol of gas in an open-end manometer. The external pressure is 1.0 bar and the temperature is 300K. In the box, sketch the manometer and qualitatively show the effect on the gas if the external pressure increases to 2.0 bar and the temperature is increased to 600K.



External pressure increases by a factor of 2. According to Boyle's law, this means the volume of the gas should be compressed to half its original volume. However, the temperature is raised by a factor of 2. According to Charles' Law, this means the volume of the gas should be double its original volume. Putting these two effects together means there is **NO OVERALL CHANGE** in the volume of the sample gas!

#2. (10 points) 15.0 kg of ammonium nitrate decomposes to nitrogen, oxygen, and water vapour.

NOTE: This question (Silberberg 4.102) was covered in DGD#3

a) What is the total volume of gas (in L) that will form at 307°C and 1.01 bar?

Balanced equation: $2\text{NH}_4\text{NO}_3(\text{s}) \rightarrow 2\text{N}_2(\text{g}) + \text{O}_2(\text{g}) + 4\text{H}_2\text{O}(\text{g})$

$$\begin{aligned} ? \text{ mol gas} &= 15.0 \text{ kg NH}_4\text{NO}_3 \times \frac{1000 \text{ g}}{\text{kg}} \times \frac{\text{mol NH}_4\text{NO}_3}{80.05 \text{ g NH}_4\text{NO}_3} \times \frac{7 \text{ mol gas}}{2 \text{ mol NH}_4\text{NO}_3} \\ &= 655.8 \text{ mol} \end{aligned}$$

$$? \text{ L gas} = \frac{(655.8 \text{ mol})(0.083145 \text{ L} \cdot \text{bar}/\text{mol} \cdot \text{K})(580 \text{ K})}{1.01 \text{ bar}} = 3.13 \times 10^4 \text{ L}$$

Answer: 3.13x10⁴ L

b) What is the partial pressure of nitrogen in the product mixture?

$$\begin{aligned} P_{\text{N}_2} &= \chi_{\text{N}_2} P_{\text{TOTAL}} \\ &= \frac{2 \text{ mol N}_2}{7 \text{ mol gas}} \times 1.01 \text{ bar} \\ &= 0.289 \text{ bar} \end{aligned}$$

Answer: 0.289 bar

#3. (10 points) A calorimeter contains 24.0 mL of water at 13.0°C. When 2.20 g of X (molar mass 47.0 g/mol) is added, it dissolves via the reaction: $X(s) \rightarrow X(aq)$ and the temperature of the solution increases to 28.0°C.

NOTE: This question is from the 2011 Midterm #1

- a) Calculate the enthalpy change for the dissolution, in kJ/mol. You may assume the specific heat capacity and density of the solution are equal to those of pure water; however, you may NOT assume that the mass of the solution is equal to the mass of the water.

$$\begin{aligned}
 q_{\text{soln}} &= m_{\text{soln}} c_{\text{soln}} \Delta T_{\text{soln}} \\
 &= (2.20\text{g} + 24.0\text{g})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})(28.0^\circ\text{C} - 13.0^\circ\text{C}) \\
 &= +1644 \text{ J} \\
 \therefore q_{\text{rxn}} &= -1644 \text{ J} \\
 \Delta H^\circ_{\text{rxn}} &= \frac{? \text{ kJ}}{\text{mol}} = \frac{-1644 \text{ J}}{2.20 \text{ g}} \times \frac{47.0 \text{ g}}{\text{mol}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = -35.1 \text{ kJ/mol}
 \end{aligned}$$

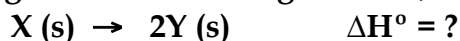
Answer: -35.1 kJ/mol

- b) Calculate the internal energy change for the dissolution, in kJ/mol.

$$\begin{aligned}
 \Delta U &= q + W = \Delta H + W \\
 \text{But: there are no gases involved. Therefore } W &\sim 0 \text{ and thus:} \\
 \Delta U &\sim \Delta H = -35.1 \text{ kJ/mol}
 \end{aligned}$$

Answer: -35.1 kJ/mol

- c) Determine the enthalpy change for the following reaction, using the provided data.



$Y(s) \rightarrow Y(aq)$	$\Delta H^\circ = +24.7 \text{ kJ}$
$2 Y(aq) \rightarrow X(aq)$	$\Delta H^\circ = -1.44 \text{ kJ}$

Using the value from part (a):

① (same)	$X(s) \rightarrow X(aq)$	$\Delta H^\circ = -35.1 \text{ kJ}$
③ reversed	$X(aq) \rightarrow 2 Y(aq)$	$\Delta H^\circ = +1.44 \text{ kJ}$
② reversed, x2	$2 Y(aq) \rightarrow 2 Y(s)$	$\Delta H^\circ = -49.4 \text{ kJ}$
SUM	$X(s) \rightarrow 2Y(s)$	$\Delta H^\circ = -83.2 \text{ kJ}$

Answer: -83.1 kJ

#4. (10 points) Dr. Fox's favourite single malt scotch whisky is *Lagavulin*, which is 43% ethanol (C_2H_5OH) by volume. While marking midterms, Dr. Fox drinks 30 mL of the scotch, of which 22% of the ethanol by mass is absorbed into her blood.

NOTE: This question is a reworded version of Suggested Silberberg problem 12.152

- a) If Dr. Fox has 6.5 L of blood, what concentration (in g/mL) of ethanol is in her blood? (*d* of ethanol = 0.789 g/mL)

Let "EtOH" represent ethanol.

$$\begin{aligned} ? \text{ g EtOH absorbed} &= 30 \text{ mL scotch} \times \frac{43 \text{ mL EtOH}}{100 \text{ mL scotch}} \times \frac{0.789 \text{ g EtOH}}{\text{mL EtOH}} \times \frac{22 \text{ g EtOH absorbed}}{100 \text{ g EtOH consumed}} \\ &= 2.24 \text{ g} \\ \frac{? \text{ g EtOH absorbed}}{\text{mL blood}} &= \frac{2.24 \text{ g EtOH absorbed}}{6.5 \text{ L blood}} \times \frac{1 \text{ L}}{1000 \text{ mL}} \\ &= 3.4 \times 10^{-4} \text{ g/mL} \end{aligned}$$

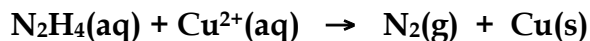
Answer: 3.4x10⁻⁴ g/mL

- b) What volume (mL) of scotch would raise Dr. Fox's blood alcohol level to 8.0×10^{-4} g/mL, the level at which she would be considered intoxicated and no longer able to mark midterms?

$$\begin{aligned} ? \text{ g EtOH absorbed} &= 6.5 \text{ L blood} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{8.0 \times 10^{-4} \text{ g EtOH absorbed}}{\text{mL blood}} \\ &= 5.20 \text{ g} \\ ? \text{ mL scotch} &= 5.20 \text{ g EtOH absorbed} \times \frac{100 \text{ g EtOH consumed}}{22 \text{ g EtOH absorbed}} \times \frac{\text{mL EtOH}}{0.789 \text{ g EtOH}} \times \frac{100 \text{ mL scotch}}{43 \text{ mL EtOH}} \\ &= 70 \text{ mL scotch} \end{aligned}$$

Answer: 70 mL

#5. (10 points) The following reaction is one route to solid copper metal.



NOTE: This question was modified from Sapling Assignment #2 + an in-class question from Chapter 3

a) Determine the overall balanced redox equation in basic solution.

	OXIDATION	REDUCTION
Balance all except O/H.	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance O with H_2O	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance H with H^+	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}^+$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Neutralize H^+ with OH^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}^+ + 4\text{OH}^-$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Simplify	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance charge with e^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^-$	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
Equalize the # of e^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^-$	$2\text{Cu}^{2+} + 4e^- \rightarrow 2\text{Cu}$

Adding the 2 half-reactions gives:



reducing agent

oxidizing agent

b) Label the oxidizing agent and reducing agent.

c) 1.54 g of N_2H_4 (MM = 32.05 g/mol) are added to 50.0 mL of a 1.55 M copper (II) hydroxide solution. What is the volume of nitrogen gas produced, at 1.01 bar and 20.0°C?

$$? \text{ mol N}_2 \text{ from N}_2\text{H}_4 = 1.54 \text{ g N}_2\text{H}_4 \times \frac{1 \text{ mol N}_2\text{H}_4}{32.05 \text{ g}} \times \frac{1 \text{ mol N}_2}{1 \text{ mol N}_2\text{H}_4} = 0.0480 \text{ mol}$$

$$? \text{ mol N}_2 \text{ from Cu}^{2+} = 0.0500 \text{ L} \times \frac{1.55 \text{ mol Cu(OH)}_2}{\text{L}} \times \frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu(OH)}_2} \times \frac{1 \text{ mol N}_2}{2 \text{ mol Cu}^{2+}} = 0.0388 \text{ mol}$$

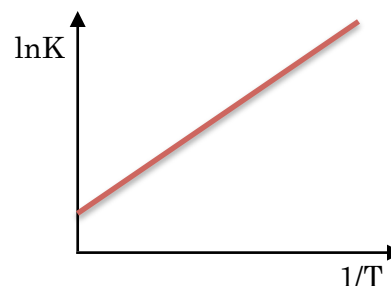
Therefore, Cu^{2+} is the limiting reagent and 0.0388 mol of nitrogen gas are formed.

$$V = \frac{nRT}{P} = \frac{(0.0388 \text{ mol})(0.083145 \text{ L} \cdot \text{bar/mol} \cdot \text{K})(293 \text{ K})}{1.01 \text{ bar}} = 0.936 \text{ L}$$

Answer: 0.936 L

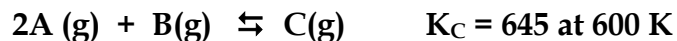
1. (10 points) Short Answer Questions

- a. On the axes provided at right, draw the expected line (or curve) of a van't Hoff plot for an exothermic reaction.



A straight line with positive slope

- b. Exactly 2.00 mol of A, 2.00 mol of B, and 2.00 mol of C are placed in a sealed 1.00 L flask at 600K.



The reaction will proceed towards (circle one) **REACTANTS** **PRODUCTS**

because $Q = [C]/[A]^2[B] = 2/(2^2 \cdot 2) = 0.25 < K \dots$ means there's too much reactant.

- c. The equivalence point of a titration is the point at which the indicator changes colour.

TRUE

FALSE

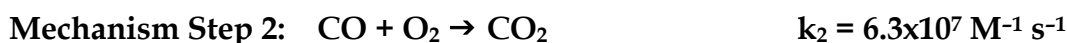
- d. If the equilibrium constant for the reaction $HA + H_2O \rightleftharpoons H_3O^+ + A^-$ is K_a , then the equilibrium constant for the reaction $H_3O^+ + A^- \rightleftharpoons HA + H_2O$ would be

K_a K_w/K_a **$1/K_a$** K_b

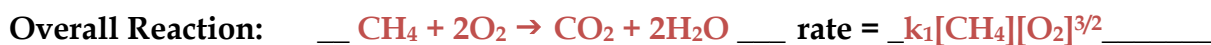
- e. For the majority of reactions, reaction rate is fastest when:

E_a high, T low E_a high, T high E_a low, T low **E_a low, T high**

- f. From the given mechanism, what is the overall reaction and its expected rate law?



Notice that, while the overall reaction works, the individual steps aren't balanced - indicating that there is something wrong with the proposed mechanism. In fact, I actually grabbed this problem from an old exam question where Part (b) of the question was: "ok, it's wrong...now go fix it so it works". So, if you went ahead and did this, then you'll also get the points. Once "fixed", it looks like this:



Both answers will be marked as correct!

- g. A buffer solution is prepared from 0.450 M HCN and 0.450 M NaCN. The pH of this solution is = $pK_a = 9.21$ _____.

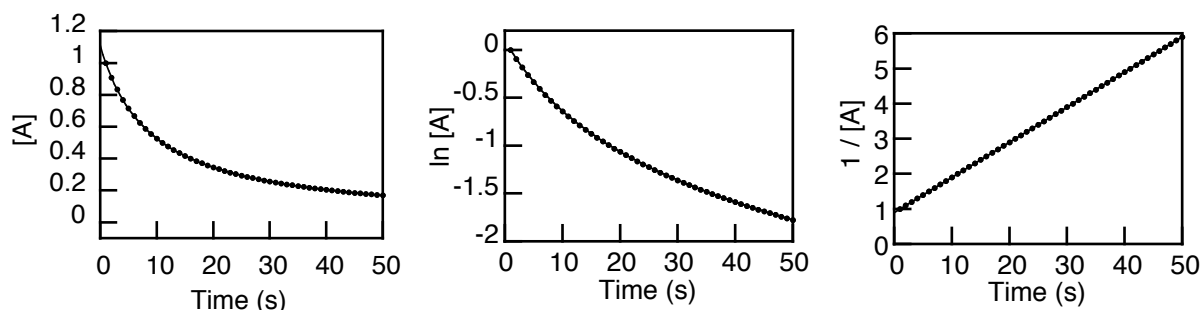
BONUS:

Classify the following as either Brønsted or Arrhenius bases.

	Brønsted	Arrhenius
NH ₃	NH ₃ NaOH PO ₄ ³⁻	NaOH
NaOH		
PO ₄ ³⁻		

Note: All of them are proton donors, so they all count as Brønsted bases. However, only NaOH actually “contains” OH⁻, so it’s the only one that is considered an Arrhenius base.

2. The progress of the reaction below is followed for 50 seconds at 298 K.



NOTE: THIS QUESTION IS TAKEN FROM THE 2010 FINAL EXAM

a). (1 point) What is the order of the reaction? second order

b). (3 points) What is the rate constant for this reaction at this temperature?

$k = \text{slope of the graph of } 1/[A] \text{ vs. time}$

$$\therefore k = \Delta y / \Delta x$$

$$= (6 \text{ M}^{-1} - 1 \text{ M}^{-1}) / (50 \text{ s} - 0 \text{ s})$$

$$= 5 \text{ M}^{-1} / 50 \text{ s}$$

$$= 0.10 \text{ M}^{-1} \text{ s}^{-1}$$

Answer: 0.10 M⁻¹ s⁻¹

c). (3 points) What is the half-life of this reaction?

$$[A]_t = 0.5[A]_0 \text{ when } t = t_{1/2}$$

$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt \quad \therefore \frac{1}{0.5[A]_0} = \frac{1}{[A]_0} + kt_{1/2}$$

$$\therefore t_{1/2} = \frac{1}{k[A]_0} = \frac{1}{(0.10 \text{ M}^{-1} \cdot \text{s}^{-1})(1.1 \text{ M})} = 9.1 \text{ s}$$

Note: this can also be done graphically, by looking at 50% decay of graph #1

Answer: 9.1 s

d). (3 points) What will [A] be after 30 seconds if its initial concentration is 0.755 M?

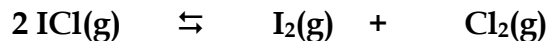
$$\frac{1}{[A]_t} = \frac{1}{[A]_0} + kt = \frac{1}{(0.755 \text{ M})} + (0.10 \text{ M}^{-1} \cdot \text{s}^{-1})(30 \text{ s})$$

$$\therefore \frac{1}{[A]_t} = 4.32 \text{ M}^{-1}$$

$$\therefore [A]_t = 0.23 \text{ M}$$

Answer: 0.23 M

3. In an analysis of interhalogen reactivity, 0.500 mol of ICl was placed in a 5.00 L flask, where it decomposed at 800K:



- a) (5 points) What are the equilibrium concentrations of each species? $K_C = 0.110$ at 800K

NOTE: THIS QUESTION IS SILBERBERG SUGGESTED PROBLEM 15.53

$$[\text{ICl}]_{\text{initial}} = (0.500 \text{ mol})/5.00 \text{ L} = 0.100 \text{ M}$$

	ICl	\rightleftharpoons	I ₂ (g) + Cl ₂ (g)
I	0.100		0
C	-2x		+x
E	0.100 - 2x		x

$$K_C = \frac{[\text{I}_2][\text{Cl}_2]}{[\text{ICl}]^2}$$

$$0.110 = \frac{x^2}{(0.100 - 2x)^2}$$

Take the square root of both sides:

$$\sqrt{0.110} = \frac{x}{0.100 - 2x}$$

$$x = 0.020 \text{ M}$$

$$\therefore [\text{ICl}]_{\text{eqm}} = 0.100 \text{ M} - 2(0.020 \text{ M}) = 0.060 \text{ M}$$

$$[\text{ICl}] = \underline{0.060 \text{ M}} \quad [\text{I}_2] = \underline{0.020 \text{ M}} \quad [\text{Cl}_2] = \underline{0.020 \text{ M}}$$

- b) (5 points) Using the data above and below, find the value of K_P for the indicated reaction.

Reaction	K_P
$\text{HCl(g)} \rightleftharpoons \frac{1}{2} \text{H}_2(\text{g}) + \frac{1}{2} \text{Cl}_2(\text{g})$	2.54
$2 \text{ICl(g)} + \text{H}_2(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + 2\text{HCl(g)}$?

Convert K_C to K_P for the equilibrium from part (a):

$$\textcircled{1} \quad 2 \text{ICl(g)} \rightleftharpoons \text{I}_2(\text{g}) + \text{Cl}_2(\text{g}) \quad K_{P1} = K_C(RT)^{\Delta n} = 0.110(0.083145 \cdot 800)^{2-2} = 0.110$$

Take the equilibrium above, reverse it and double it:

$$\textcircled{2} \quad \text{H}_2(\text{g}) + \text{Cl}_2(\text{g}) \rightleftharpoons 2 \text{HCl(g)} \quad K_{P2} = (1/2.54)^2 = 0.155$$

Now add equations $\textcircled{1}$ and $\textcircled{2}$ together:

$$\textcircled{3} \quad 2 \text{ICl(g)} + \text{H}_2(\text{g}) \rightleftharpoons \text{I}_2(\text{g}) + 2\text{HCl(g)} \quad K_{P3} = K_{P1} \cdot K_{P2} = (0.110)(0.155) = 0.017$$

$$\text{Answer: } \underline{0.017}$$

4. A certain New Mexico chemistry teacher (let's call him "Heisenberg") decides to supplement his income by synthesizing and selling methamphetamine, $C_{10}H_{15}N$ (MM = 149.2 g/mol). To ship it undetected, he disguises it by creating aqueous solutions (meth has an aqueous solubility of 0.11 g/100 mL).

NOTE: THIS QUESTION IS TAKEN FROM MIDTERM #2 2011

- a) (6 points) A saturated solution of this compound has a pH = 10.08. What is the value of K_b ?

Let B represent methamphetamine.

$$? \frac{\text{mol B}}{\text{L}} = \frac{0.11 \text{ g}}{100 \text{ mL}} \times \frac{1000 \text{ mL}}{\text{L}} \times \frac{\text{mol B}}{149.2 \text{ g}} = 7.37 \times 10^{-3} \text{ mol/L}$$

$$\text{pH} = 10.08$$

$$\text{pOH} = 14 - 10.08 = 3.92$$

$$\therefore [\text{H}_3\text{O}^+] = 10^{-3.92} = 1.20 \times 10^{-4} \text{ mol/L}$$

	B	+	H ₂ O	⇌	BH ⁺	+	OH ⁻
I	0.00737		-		0		0
C	-0.00012		-		+0.00012		+0.00012
E	0.00725		-		0.00012		0.00012

$$K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]} = \frac{(0.00012)(0.00012)}{0.00725} = 2.0 \times 10^{-6}$$

- b) (4 points) Ammonia, NH_3 , has a K_b of 1.8×10^{-5} . On the equilibrium below, label the acid, base, conjugate acid and conjugate base, and predict the preferred direction of the reaction (i.e. towards reactants or products?). To obtain full marks, show your reasoning.



$$K_b \text{ of } C_{10}H_{15}N \text{ is } 2.0 \times 10^{-6}$$

$$K_b \text{ of } NH_3 \text{ is } 1.8 \times 10^{-5}$$

That means ammonia is a better proton acceptor than methamphetamine.

Therefore, the reaction goes TOWARDS THE REACTANTS.

5. Your TA informs you that you will be performing a titration of 25.00 mL of 0.100 M acetic acid with 0.100 M NaOH.

NOTE: THIS IS A NEW QUESTION, BUT IT'S NEARLY IDENTICAL TO WHAT I COVERED IN CLASS AND IN THE DGD

- a) (3 points) What is the initial pH (before any NaOH is added)?

Let HA represent the weak acid.

	HA	+	H ₂ O	⇌	H ₃ O ⁺	+	A ⁻
I	0.100		-		0		0
C	-x		-		+x		+x
E	0.100 - x		-		x		x

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5}$$

$$\frac{x^2}{0.100} \approx 1.8 \times 10^{-5}$$

$$\therefore x \approx 0.00134 \text{ M} = [\text{H}_3\text{O}^+] \quad \text{Check: } \frac{0.00134}{0.100} \times 100\% = 1.3\% \longrightarrow \text{PASSES ASSUMPTION}$$

$$\text{pH} = -\log(0.00134) = 2.87$$

Answer: 2.87

- b) (3 points) What is the pH at the half-equivalence point?

At the half-equivalence point, exactly HALF of the acetic acid has been converted to its conjugate base, acetate. Therefore, the solution contains equal concentrations of CH₃COOH and CH₃COO⁻: this is a buffer!

Thus, at the half-equivalence point:

$$\begin{aligned} \text{pH} &= \text{pKa} - \log\left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}\right) \\ &= \text{pKa} \\ &= -\log(1.8 \times 10^{-5}) \\ &= 4.74 \end{aligned}$$

**Note: This can also be solved the "long way" as follows:

$$\text{mol HA} = (0.100 \text{ mol/L})(0.025 \text{ L}) = 0.00250 \text{ mol}$$

$$\therefore \text{mol OH}^- \text{ added} = \frac{1}{2}(\text{mol HA}) = 0.00125 \text{ mol} \quad (\text{this corresponds to adding 12.5 mL of base})$$

	HA	+	OH ⁻	→	A ⁻	+	H ₂ O
Before	0.00250				0		-
Addition			0.00125				-
Modification	-0.00125		-0.00125		+0.00125		-
After	0.00125		0		0.00125		

$$\text{new } [\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}] = 0.00125 \text{ mol} / (0.0250 \text{ L} + 0.0125 \text{ L}) = 0.0333 \text{ M}$$

This is a buffer (passes both criteria) → substituting into the H-H equation gives the same value as above.

Answer: 4.74

- c) (4 points) Which of the following indicators is an appropriate choice for this titration? Show your calculations or explain your reasoning to obtain full marks.

Indicator	pH Range
Thymol Blue	8 to 10
Bromocresol Green	4 to 6
Methyl Violet	0 to 2

At the equivalence point, ALL of the acid has been converted to the conjugate base, A^- . However, A^- is the conjugate base of a weak acid, and so it is a *good proton acceptor*, meaning it will act as a base (it will hydrolyze):



Therefore, the pH will be basic at the equivalence point, and we will need an indicator that changes colour at a basic pH. From the list, Thymol Blue makes the best choice!

***Again, note that this can be solved the “long way” as follows:

mol HA = mol OH^- added = 0.00250 mol (this corresponds to adding 25.0 mL of base)

	HA	+	OH^-	\rightarrow	A^-	+	H_2O
Before	0.00250				0		-
Addition			0.00250				-
Modification	-0.00250		-0.00250		+0.00250		-
After	0		0		0.00250		

new $[A^-] = 0.00250 \text{ mol} / (0.0250 \text{ L} + 0.0250 \text{ L}) = 0.0500 \text{ M}$

This is no longer a buffer: it's just a 0.0500 M solution of acetate, which acts as a base:

	A^-	+	H_2O	\rightleftharpoons	HA	+	OH^-
I	0.050		-		0		0
C	-x		-		+x		+x
E	0.050 - x		-		x		x

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{[HA][OH^-]}{[A^-]}$$

$$5.6 \times 10^{-10} = \frac{x^2}{0.0500 - x}$$

$$\frac{x^2}{0.0500} \approx 5.6 \times 10^{-10}$$

$$\therefore x \approx 5.3 \times 10^{-6} \text{ M} = [OH^-] \quad \text{Check: } \frac{5.3 \times 10^{-6}}{0.0500} \times 100\% = 0.01\% \longrightarrow \text{PASSES ASSUMPTION}$$

$$\text{pH} = 14 - \text{pOH} = 14 - \{-\log(5.6 \times 10^{-6})\} = 8.75$$

Basic pH \rightarrow Thymol Blue is the best choice.

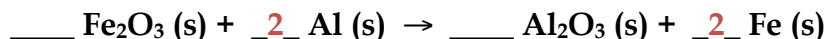
Answer: Thymol Blue

1. (20 points) Short Answer Questions.

a) Give the name or formula for the following compounds:

Tin (II) oxide SnOSulfurous acid H₂SO₃

b) Balance the following reaction:

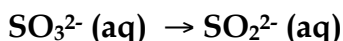


When 50.00 g of iron (III) oxide was reacted with excess aluminum, 28.65 g of solid iron was formed. The percent yield of the reaction is 81.9%.

$$? \text{ g Fe theoretical} = 50.00 \text{ g Fe}_2\text{O}_3 \times \frac{\text{mol Fe}_2\text{O}_3}{159.7 \text{ g Fe}_2\text{O}_3} \times \frac{2 \text{ mol Fe}}{1 \text{ mol Fe}_2\text{O}_3} \times \frac{55.85 \text{ g Fe}}{\text{mol Fe}} = 34.97 \text{ g}$$

$$\% \text{ yield} = \frac{28.65 \text{ g}}{34.97 \text{ g}} \times 100\% = 81.9\%$$

c) Determine if the following half-reaction (in acidic solution) is an oxidation or a reduction and the number of electrons gained/lost in the process.



OXIDATION REDUCTION # of electrons = 2

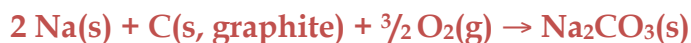
There are three ways to solve this problem:

i. Using ox. states: S goes from +4 to +2 → this is a reduction

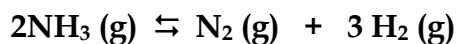
ii. Balancing the half-reaction: $2\text{H}^+ + \text{SO}_3^{2-} + 2\text{e}^- \rightarrow \text{SO}_2^{2-} + \text{H}_2\text{O}$

Since the electrons are reactants, this is a reduction

iii. The “oxygen content” of the ion decreases; this is a reduction

d) The standard heat of formation of one mole of solid sodium carbonate is -1 131 kJ. Write the chemical equation for the reaction to which this value applies.e) Under constant pressure conditions, the heat absorbed/released by a chemical reaction is equal to: ΔU ΔH 0 qv w

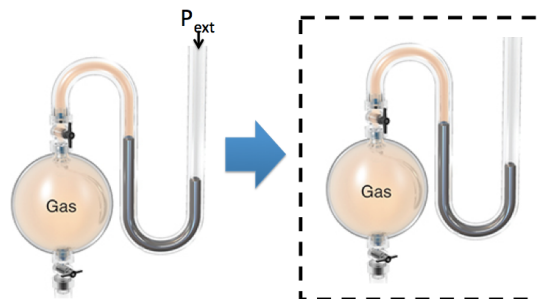
f) For the following reaction



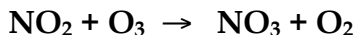
the value of K_c is 2.8×10^{-9} at 298 K. Therefore, K_p for this reaction is 1.7×10^{-6} .

$$K_P = K_C(RT)^{\Delta n} = (2.8 \times 10^{-9})(0.083145 \cdot 298)^{4-2} = 1.7 \times 10^{-6}$$

- g) The figure on the left shows 1 mol of gas in an open-end manometer. The external pressure is 1.0 bar and the temperature is 300K. In the box, sketch the manometer and qualitatively show the effect on the gas if the external pressure increases to 2.0 bar and the temperature is increased to 600K.



- h) Determine the rate law and value of k for the following reaction using the data provided.



$[\text{NO}_2]_i$ (M)	$[\text{O}_3]_i$ (M)	Initial rate (M/s)
0.10	0.33	1.42
0.10	0.66	2.84
0.25	0.66	7.10

Rate Law = $\underline{k[\text{NO}_2][\text{O}_3]}$

Value of k : $\underline{43.0 \text{ M}^{-1} \text{ s}^{-1}}$

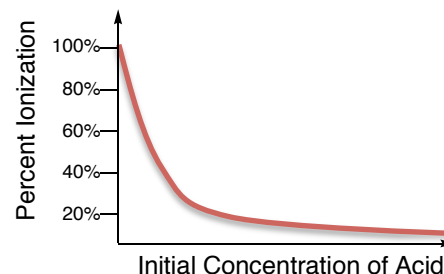
- i) Name two factors that influence the speed of a chemical reaction:

i. temperature, concentration, E_a , catalysts, surface area, etc.

ii. _____

- j) The conjugate acid and conjugate base of H_2PO_4^- are H_3PO_4 and HPO_4^{2-} , respectively.

- k) On the axes provided, draw a line (or curve) representing the percent ionization of a weak acid as a function of the initial concentration of the acid.



- l) The mixing of one of these pairs of reactants will result in a precipitation reaction. Indicate the correct pair and give the formula of the expected precipitate.

i. K_2SO_4 (aq) + $\text{Cu}(\text{NO}_3)_2$ (aq)

ii. $\text{Ba}(\text{NO}_3)_2$ (aq) + Na_2CO_3 (aq) Precipitate: BaCO_3

iii. NaClO_4 (aq) + $(\text{NH}_4)_2\text{S}$ (aq)

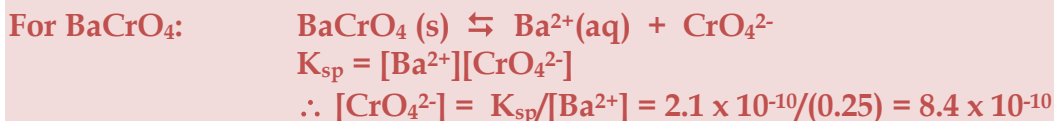
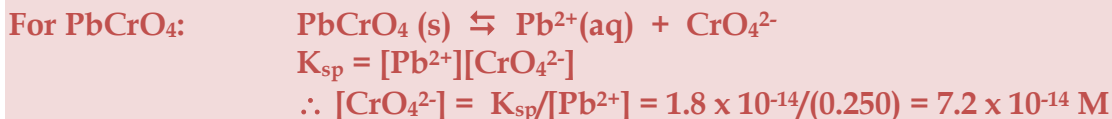
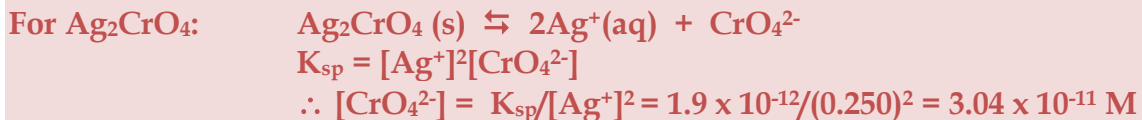
- m) The maximum number of electrons that can have the designation $3p$ is 6.

- n) Cesium's outermost electron is in an orbital with quantum numbers $n = 6$, $\ell = 0$, $m_\ell = 1$.

TRUE FALSE

2. You are given 200.0 mL of an aqueous solution that contains 0.250 M each of Ag^+ , Pb^{2+} and Ba^{2+} . You wish to precipitate these cations sequentially by adding chromate to the solution.
- a) (4 points) In what order will the solids precipitate as chromate is added to the above solution?

What are the concentrations of CrO_4^{2-} needed to precipitate each cation? Whichever requires the least amount will precipitate first...



First = PbCrO_4 Second = Ag_2CrO_4 Third = BaCrO_4

- b) (2 points) What concentration of chromate will cause the first precipitation?

From part (a), the concentration at which precipitation of PbCrO_4 begins is $7.2 \times 10^{-14} \text{ M}$.

Answer: $7.2 \times 10^{-14} \text{ M}$

- c) (4 points) At the point *just before* BaCrO_4 begins to precipitate, what will be the concentration of all of the ions in solution?

BaCrO_4 begins to precipitate when the $[\text{CrO}_4^{2-}] = 8.4 \times 10^{-10} \text{ M}$. At this concentration, both Ag_2CrO_4 and PbCrO_4 have precipitated. Therefore, what are the concentrations of each ion when $[\text{CrO}_4^{2-}] = 8.4 \times 10^{-10} \text{ M}$?

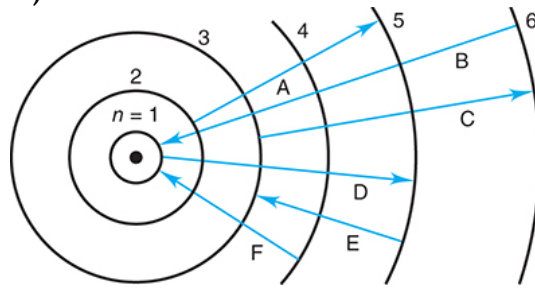
$[\text{Ba}^{2+}]$ 0.250 M (still not precipitated)

$[\text{Ag}^+]$ $K_{\text{sp}} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$
 $\therefore [\text{Ag}^+] = \{K_{\text{sp}}/[\text{CrO}_4^{2-}]\}^{1/2} = \{1.9 \times 10^{-12}/(8.4 \times 10^{-10})\}^{1/2} = 0.0476 \text{ M}$

$[\text{Pb}^{2+}]$ $K_{\text{sp}} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}]$
 $\therefore [\text{Pb}^{2+}] = K_{\text{sp}}/[\text{CrO}_4^{2-}] = 1.8 \times 10^{-14}/(8.4 \times 10^{-10}) = 2.14 \times 10^{-5} \text{ M}$

$[\text{Ag}^+] = 0.0476 \text{ M}$ $[\text{Pb}^{2+}] = 2.14 \times 10^{-5} \text{ M}$ $[\text{Ba}^{2+}] = 0.250 \text{ M}$

3. A Bohr-model representation of the H atom is shown below, with several transitions depicted by arrows. (Note: not to scale)



- a) (2 points) Which transitions are absorptions, and which are emissions?

Absorptions ($n_f > n_i$): A, C, D
Emissions ($n_f < n_i$): B, E, F

- b) (3 points) Rank the absorptions in terms of increasing energy.

According to the Bohr Equation, the change in energy is proportional to $-[(1/n_f^2) - (1/n_i^2)]$.

Absorption A:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{5^2} - \frac{1}{2^2}\right) = 0.21$$

Absorption C:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{6^2} - \frac{1}{3^2}\right) = 0.08$$

Absorption D:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{5^2} - \frac{1}{1^2}\right) = 0.96$$

Therefore, the order is: $C < A < D$.

- c) (3 points) Rank the emissions in terms of increasing wavelength of light emitted.

According to the Bohr Equation, the change in energy is proportional to $-[(1/n_f^2) - (1/n_i^2)]$.

Emission B:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{6^2} - \frac{1}{1^2}\right) = -0.97$$

Emission E:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{5^2} - \frac{1}{3^2}\right) = -0.07$$

Emission F:

$$\Delta E \propto -\left(\frac{1}{n_f^2} - \frac{1}{n_i^2}\right) = -\left(\frac{1}{4^2} - \frac{1}{1^2}\right) = -0.94$$

ΔE is inversely proportional to wavelength.
 Therefore, the order is: $B < F < E$.

- d) (2 points) This model does not work for any element other than hydrogen. Briefly explain why.

Bohr's model accounts for only one force: the attraction between the single proton and the single electron in hydrogen. It does not account for the inter-electronic repulsion between electrons in all other elements.

4. You wish to prepare a 100 mL solution that is 0.0100 M MgCl_2 and also 0.100 M NH_3 . You have access to solid MgCl_2 and a concentrated stock solution of 2.88 M NH_3 .
- a) (4 points) Determine the mass of MgCl_2 and the volume of NH_3 you need to prepare your solution.

$$? \text{ g MgCl}_2 = 100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.0100 \text{ mol MgCl}_2}{\text{L}} \times \frac{95.2 \text{ g MgCl}_2}{\text{mol MgCl}_2} = 0.0952 \text{ g}$$

$$? \text{ mL NH}_3 = \left[100 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.100 \text{ mol NH}_3}{\text{L}} \right] \times \frac{\text{L}}{2.88 \text{ mol NH}_3} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 3.47 \text{ mL}$$

mass of MgCl_2 = 0.0952 g volume of NH_3 = 3.47 mL

- b) (2 points) Your lab TA warns you that, when preparing solutions of Mg^{2+} (aq) and NH_3 (aq), a precipitate of $\text{Mg}(\text{OH})_2$ (s) may form, depending on the concentrations. Write the chemical equation and the K_{sp} expression for the formation of this precipitate.

The precipitation reaction is: $\text{Mg}^{2+}(\text{aq}) + 2 \text{OH}^- \rightarrow \text{Mg}(\text{OH})_2(\text{s})$

The K_{sp} expression for $\text{Mg}(\text{OH})_2$ is: $K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 1.2 \times 10^{-11}$

- c) (4 points) Considering the solution prepared in part (a), will you observe a precipitate? The K_{b} for ammonia is 1.8×10^{-5} . Please show your work.

The OH^- comes from the ionization of ammonia:

	NH_3	+	H_2O	\rightleftharpoons	NH_4^+	+	OH^-
I	0.100		-		0		0
C	-x		-		+x		+x
E	0.100 - x		-		x		x

$$K_{\text{b}} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = \frac{x^2}{0.100 - x} = 1.8 \times 10^{-5} \quad \text{Make the assumption: } \frac{x^2}{0.100} \approx 1.8 \times 10^{-5}$$

$$\therefore x \approx 0.00134 \text{ M} = [\text{OH}^-] \quad \text{Check: } \frac{0.00134}{0.100} \times 100\% = 1.3\% \longrightarrow \text{PASSES ASSUMPTION}$$

$$Q_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = (0.0100 \text{ M})(0.00134 \text{ M})^2 = 1.8 \times 10^{-8}$$

Since $Q_{\text{sp}} > K_{\text{sp}}$, there will be precipitation.

Answer (circle one):

YES

NO

5. The total amount of sulfur released into the atmosphere per year by the burning of coal is about 75 million metric tonnes (1000 kg = 1 t).

a) (5 points) Assuming this were all solid sulfur, how big a cube would this occupy? Find the dimension of each side of the cube in metres. The density of sulfur is 2.0 g/cm³.

$$? \text{ m}^3 \text{ S} = 75 \times 10^6 \text{ t} \times \frac{1000 \text{ kg}}{1 \text{ t}} \times \frac{1000 \text{ g}}{1 \text{ kg}} \times \frac{1 \text{ cm}^3}{2.0 \text{ g S}} \times \frac{1 \text{ m}^3}{10^6 \text{ cm}^3} = 3.75 \times 10^7 \text{ m}^3$$

$$V = d^3$$

$$\therefore d = \sqrt[3]{V} = \sqrt[3]{3.75 \times 10^7 \text{ m}^3} = 335 \text{ m}$$

Answer: _____ **335 m** _____

b) (5 points) A rare but stable isotope of sulfur is sulfur-33, with a percent natural abundance of only 0.75%. How many atoms of sulfur-33 would be present in the cube of part (a)?

$$? \text{ atoms } ^{33}\text{S} = 75 \times 10^6 \text{ t S} \times \frac{1000 \text{ kg S}}{1 \text{ t S}} \times \frac{1000 \text{ g S}}{1 \text{ kg S}} \times \frac{\text{mol S}}{32.066 \text{ g S}} \times \frac{0.75 \text{ mol } ^{33}\text{S}}{100 \text{ mol S}} \times \frac{6.022 \times 10^{23} \text{ atoms } ^{33}\text{S}}{\text{mol } ^{33}\text{S}}$$

$$= 1.06 \times 10^{34} \text{ atoms } ^{33}\text{S}$$

Answer: _____ **1.06x10³⁴ atoms** _____

6. Methanol, CH₃OH, is synthesized directly on the industrial scale by the reaction of carbon monoxide with hydrogen gas.

a) (1 point) Write a balanced chemical equation for this reaction.



b) (3 points) Using the data below, what is the value for the enthalpy change of the reaction of part (a) at 25°C?

	ΔH_f° (kJ/mol)
CO(g)	-110.5
CO ₂ (g)	-393.5
H ₂ (g)	0.0
H ₂ O(g)	-241.8
CH ₃ OH(g)	-200.7
CH ₄ (g)	-74.87

$$\begin{aligned} \Delta H^\circ_{\text{rxn}} &= \sum(\Delta H_f^\circ \text{ products}) - \sum(\Delta H_f^\circ \text{ reactants}) \\ &= [\Delta H_f^\circ \{\text{CH}_3\text{OH(g)}\}] - [\Delta H_f^\circ \{\text{CO(g)}\} + 2 \times \Delta H_f^\circ \{\text{H}_2\text{(g)}\}] \\ &= [(-220.7)] - [(-110.5) + (2 \times 0)] \text{ kJ/mol} \\ &= -90.2 \text{ kJ/mol} \end{aligned}$$

Answer: - 90.2 kJ/mol

c) (4 points) The value of the equilibrium constant for the above reaction at 298 K is 2.27×10^4 . Calculate the value of the equilibrium constant at 500 K.

$$\begin{aligned} K_1 &= 2.27 \times 10^4 && @ T_1 = 298 \text{ K} \\ K_2 &= ? && @ T_2 = 500 \text{ K} \end{aligned}$$

Using the van't Hoff Equation:

$$\begin{aligned} \ln\left(\frac{K_2}{K_1}\right) &= -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right) \\ \ln\left(\frac{K_2}{2.27 \times 10^4}\right) &= -\frac{-90\,200 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}}\right) \\ \therefore K_2 &= 9.31 \times 10^{-3} \end{aligned}$$

Answer: 9.31x10⁻³

d) (2 points) Based on your answer in part (c), what effect does changing the temperature from 298 K to 500 K have on the equilibrium?

The reaction is exothermic; therefore, increasing temperature shifts the equilibrium towards the reactants and the value of K thus decreases.

7. When Dr. Fox goes scuba diving, she uses NITROX, a special blend of enriched air that allows for more repetitive dives by reducing the build-up of nitrogen in the blood (that way, she won't get "the bends"!). The local scuba shop prepares 5.00 L tanks of NITROX by mixing 26.0 g of O₂ with 44.2 g of N₂ at a temperature of 25.0°C.

a) What is the mole fraction of each gas in the mixture?

$$? \text{ mol O}_2 = 26.0 \text{ g O}_2 \times \frac{\text{mol O}_2}{31.998 \text{ g O}_2} = 0.812 \text{ mol O}_2$$

$$? \text{ mol N}_2 = 44.2 \text{ g N}_2 \times \frac{\text{mol N}_2}{28.014 \text{ g N}_2} = 1.578 \text{ mol N}_2$$

$$\text{Total mol } n_T = 0.812 + 1.578 = 2.39 \text{ mol}$$

$$\therefore \chi_{\text{N}_2} = \frac{1.578 \text{ mol}}{2.39 \text{ mol}} = 0.660$$

$$\therefore \chi_{\text{O}_2} = \frac{0.812 \text{ mol}}{2.39 \text{ mol}} = 0.340$$

$$\chi \text{ of N}_2 = \underline{\quad 0.660 \quad} \qquad \chi \text{ of O}_2 = \underline{\quad 0.340 \quad}$$

b) What is the partial pressure of each gas, in atm?

$$P_T = \frac{n_T RT}{V} = \frac{(2.39 \text{ mol})(0.08206 \text{ L} \cdot \text{atm/mol} \cdot \text{K})(298\text{K})}{5.00 \text{ L}}$$

$$= 11.7 \text{ atm}$$

$$P_{\text{N}_2} = \chi_{\text{N}_2} \times P_T = (0.660)(11.7 \text{ atm})$$

$$= 7.7 \text{ atm}$$

$$P_{\text{O}_2} = \chi_{\text{O}_2} \times P_T = (0.340)(11.7 \text{ atm})$$

$$= 4.0 \text{ atm}$$

$$P \text{ of N}_2 = \underline{\quad 7.7 \text{ atm} \quad} \qquad P \text{ of O}_2 = \underline{\quad 4.0 \text{ atm} \quad}$$

c) What will be the total pressure left in the tank after Dr. Fox breathes 80% of it by volume during a dive?

If 80% has been consumed, there is 20% left.

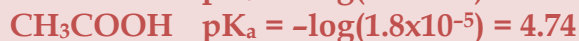
V₂ is 20% of V₁ → Therefore, P₂ is 20% of P₁

$$P_2 = (0.20)(11.7 \text{ atm}) = 2.3 \text{ atm}$$

$$P_T = \underline{\quad 2.3 \text{ atm} \quad}$$

8. You are asked to prepare a buffer solution with a pH of 5.00. Exactly 500 mL of each of the following solutions, all 0.100 M, are available to you: formic acid, acetic acid, sodium formate and sodium acetate.

a) (3 points) Which solutions would you use to prepare this buffer, and what would be the required base-to-acid ratio for a pH of 5.00?



Since the desired pH is 5.00, $\text{CH}_3\text{COOH}/\text{CH}_3\text{COO}^-$ is the more appropriate conjugate pair. The required base-to-acid ratio is thus:

$$\text{pH} = pK_a - \log \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \quad \therefore \frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} = 10^{\text{pH} - pK_a} = 10^{5.00 - 4.74} = 1.82$$

b) (3 points) As mentioned, you only have 500 mL of each 0.100 M solution. You are asked to make as much buffer as possible from the available solutions (i.e. the maximum volume possible). What would be the final total volume of the buffer? You may assume that volumes are additive.

A ratio of 1.82 indicates that there is more base than acid – therefore, we must use the max. amount of available base (all of the 500 mL provided) and then add the appropriate amount of acid to get the desired pH.

$$\text{max. mol CH}_3\text{COO}^- \text{ available} = 500 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{0.100 \text{ mol CH}_3\text{COO}^-}{\text{L}} = 0.0500 \text{ mol CH}_3\text{COO}^-$$

$$\therefore \text{required mol CH}_3\text{COOH} = 0.0500 \text{ mol CH}_3\text{COO}^- \times \frac{1 \text{ mol CH}_3\text{COOH}}{1.82 \text{ mol CH}_3\text{COO}^-} = 0.0275 \text{ mol CH}_3\text{COOH}$$

$$\therefore \text{required mL CH}_3\text{COOH} = 0.0275 \text{ mol CH}_3\text{COOH} \times \frac{\text{L}}{0.100 \text{ mol CH}_3\text{COOH}} \times \frac{1000 \text{ mL}}{1 \text{ L}} = 275 \text{ mL}$$

$$\therefore \text{total volume} = 500 \text{ mL} + 275 \text{ mL} = 775 \text{ mL}$$

Answer: 775 mL

c) (4 points) If 0.965 mL of 8.00 M $\text{Ba}(\text{OH})_2$ is added to the buffer, prepared in part (b), what will be the new pH?

$$\text{mol OH}^- \text{ added} = 0.965 \text{ mL} \times \frac{1 \text{ L}}{1000 \text{ mL}} \times \frac{8.00 \text{ mol Ba}(\text{OH})_2}{\text{L}} \times \frac{2 \text{ mol OH}^-}{1 \text{ mol Ba}(\text{OH})_2} = 0.01544 \text{ mol OH}^-$$

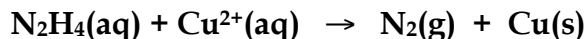
	$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$			
B	0.02750		0.05000	-
A		0.01544		-
M	-0.01544	-0.01544	+0.01544	-
A	0.01206	0	0.06544	-

This is still a buffer (it passes both criteria), so we may use the H-H equation:

$$\text{pH} = pK_a + \log \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]} \right) = 5.47$$

Answer: 5.47

9. The following reaction is one route to solid copper metal.



a) (4 points) Determine the overall balanced redox equation in basic solution.

	OXIDATION	REDUCTION
Balance all except O/H.	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance O with H_2O	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance H with H^+	$\text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}^+$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Neutralize H^+ with OH^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}^+ + 4\text{OH}^-$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Simplify	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O}$	$\text{Cu}^{2+} \rightarrow \text{Cu}$
Balance charge with e^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^-$	$\text{Cu}^{2+} + 2e^- \rightarrow \text{Cu}$
Equalize the # of e^-	$4\text{OH}^- + \text{N}_2\text{H}_4 \rightarrow \text{N}_2 + 4\text{H}_2\text{O} + 4e^-$	$2\text{Cu}^{2+} + 4e^- \rightarrow 2\text{Cu}$

Adding the 2 half-reactions gives:



reducing agent

oxidizing agent

b) (2 points) Label the oxidizing agent and reducing agent.

c) (4 points) 1.54 g of N_2H_4 (MM = 32.05 g/mol) are added to 50.0 mL of a 1.55 M copper (II) hydroxide solution. What is the volume of nitrogen gas produced, at 1.01 bar and 20.0°C?

$$? \text{ mol N}_2 \text{ from N}_2\text{H}_4 = 1.54 \text{ g N}_2\text{H}_4 \times \frac{\text{mol N}_2\text{H}_4}{32.05 \text{ g}} \times \frac{1 \text{ mol N}_2}{1 \text{ mol N}_2\text{H}_4} = 0.0480 \text{ mol}$$

$$? \text{ mol N}_2 \text{ from Cu}^{2+} = 0.0500 \text{ L} \times \frac{1.55 \text{ mol Cu(OH)}_2}{\text{L}} \times \frac{1 \text{ mol Cu}^{2+}}{1 \text{ mol Cu(OH)}_2} \times \frac{1 \text{ mol N}_2}{2 \text{ mol Cu}^{2+}} = 0.0388 \text{ mol}$$

Therefore, Cu^{2+} is the limiting reagent and 0.0388 mol of nitrogen gas are formed.

$$V = \frac{nRT}{P} = \frac{(0.0388 \text{ mol})(0.083145 \text{ L} \cdot \text{bar/mol} \cdot \text{K})(293 \text{ K})}{1.01 \text{ bar}} = 0.936 \text{ L}$$

Answer: 0.936 L