

CHM1311 E

Name : \_\_\_\_\_

TWO STAGE DGD QUIZ

October 2018

## STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. (6 pts) Hydrogen fluoride is produced industrially by the action of sulphuric acid on  $\text{CaF}_2$ . If 365 kg of  $\text{CaF}_2$  is treated with excess sulphuric acid and 155 kg of HF is produced, what is the percent yield and what mass (in kg) of  $\text{CaF}_2$  remains unreacted? The other product of the reaction is  $\text{CaSO}_4$ .

Percent Yield = \_\_\_\_\_      Mass of  $\text{CaF}_2$  = \_\_\_\_\_

2. (6 pts) Shoppers Drug Mart sells a homeopathic cough syrup (100 mL bottle for about \$8) that contains arsenic at a concentration of "14 CH". This corresponds to a ratio of 1.00 g of arsenic to  $10^{28}$  g of syrup. How many bottles of this cough syrup must you drink in order to consume one atom of arsenic? The cough syrup has a density of 2.45 g/mL.

Number of bottles = \_\_\_\_\_

3. (3 pts) Walmart sells antifreeze, an aqueous solution that is 28.6% ethylene glycol ( $C_2H_6O_2$ ) by mass. If the density of this solution is  $1.03 \text{ g/cm}^3$ , calculate its molality.

Molality = \_\_\_\_\_

LAST NAME (in CAPITAL letters): \_\_\_\_\_

FIRST NAME: \_\_\_\_\_

Student Number: \_\_\_\_\_

# CHM 1311 Midterm #1 Fall 2018

## STAGE 1 – 60 min

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 6 pages in this test. A periodic table, data tables, and a formula sheet are provided separately. Please show your work to receive partial credit.

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## 1. Short Answer Questions

- a) (1 pt) Four balloons are filled to the same volume with the following gases and a small hole is made in each balloon. Circle the one that will deflate the *fastest* and underline the one that will deflate the *slowest*.

Xe                      SO<sub>3</sub>                      O<sub>2</sub>                      CH<sub>4</sub>

- b) (1.5 pts) The standard heat of formation of solid potassium permanganate is -813.4 kJ. Write the chemical equation for the reaction to which this value applies.

- c) (0.5 pt) Which of the following is/are a state function?      q      W      ΔU      ΔH
- d) (1 pt) Starting with an atom of germanium-72, we add 3 protons, add 6 neutrons, and add 4 electrons to the atom. Fill in the blanks for our new species:

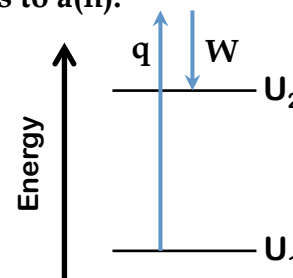
Number of protons	Number of neutrons	Number of electrons	Chemical Symbol

- e) (0.5 pt) A sample of a gas is slowly expanded from 4.0 L to 8.0 L. In order for the average kinetic energy of the gas to increase, the gas must also be simultaneously heated.

TRUE                      FALSE

- f) (0.5 pt) The energy change shown in the diagram at right corresponds to a(n):

- EXOTHERMIC CONTRACTION
- ENDOTHERMIC CONTRACTION
- EXOTHERMIC EXPANSION
- ENDOTHERMIC EXPANSION



(1 pt) BONUS:

In order to convert an empirical formula to a molecular formula, one must know/determine the \_\_\_\_\_ of the unknown compound.

2. Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is used to make other organic compounds. In concentrated sulphuric acid, ethanol forms diethyl ether and water:



In a side reaction, some ethanol forms ethylene and water:



- a) (4 pts) If 50.0 g of ethanol yields 35.9 g of diethyl ether, what is the percent yield of diethyl ether?

%Yield = \_\_\_\_\_

- b) (4 pts) If 45.0% of the ethanol that did not produce the ether reacts by the side reaction, what mass (in g) of ethylene is produced?

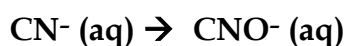
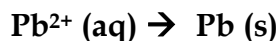
Mass = \_\_\_\_\_

- c) (2 pts) What volume (in L) does the ethylene gas (produced in part b) occupy at STP?

Volume = \_\_\_\_\_

3. A salesman comes to your door and tells you that the tap water in your neighbourhood has recently been tested and high levels of lead (Pb) have been found. He can sell you a purification device for \$7500 that can attach to your tap and remove the lead ions from the water. He wants to test your water to see if it is needed; all he needs from you is a small sample of tap water (100.0 mL).

- a) (3 pts) His test kit uses the following half reactions to test for the lead ions. Find the overall balanced redox reaction, under basic conditions (including phases).



- b) (1 pt) Identify the oxidizing agent and the reducing agent in your reaction above.
- c) (2 pts) The salesman tests 100.0 mL of your tap water, gasps, and finds that your glass of water contains 9 billion Pb ions in it ( $9.00 \times 10^9$ ) and encourages you to buy the purification device. According to his test results, what would be the mass (in mg) of lead in 1.00 L of water?

Mass = \_\_\_\_\_

- d) (1 pt) Health Canada says that concentrations of 0.01 ppm (or 0.01 mg/L) and lower are safe. Do you spend \$7500 on the purification system?

4. In class, Dr. Fox showed video of scuba diving in False Bay, South Africa, where the water temperature was a chilly  $13.5^{\circ}\text{C}$ . Despite wearing two 5 mm thick neoprene wetsuits, Dr. Fox still lost body heat at a rate of  $38.0\text{ J per second}$ .

a) (2 pts) How much body heat, in kJ, was lost over the course of a 45.0 min dive?

$$q = \underline{\hspace{10em}}$$

b) (3 pts) To recuperate this energy loss, Dr. Fox decides to eat a candy bar, which contains glucose,  $\text{C}_6\text{H}_{12}\text{O}_6$ . Using the data table, determine the enthalpy of combustion of glucose, in kJ/mol.

Substance	$\Delta H_f^{\circ}$ (kJ/mol)
$\text{CO (g)}$	-110.5
$\text{CO}_2 \text{ (g)}$	-393.5
$\text{O}_3 \text{ (g)}$	143
$\text{CH}_3\text{OH (l)}$	-238.6
$\text{C}_2\text{H}_5\text{OH (l)}$	-277.6
$\text{C}_6\text{H}_{12}\text{O}_6 \text{ (s)}$	-1273.3
$\text{C}_{12}\text{H}_{22}\text{O}_{11} \text{ (s)}$	-2221.7
$\text{H}_2\text{O (l)}$	-285.8

$$\Delta H^{\circ}_{\text{comb}} = \underline{\hspace{10em}}$$

c) (3 pts) If the candy bar contains 8.55% glucose by mass, how many grams of it will Dr. Fox need to eat to balance out the heat lost in part (a)?

$$\text{Mass} = \underline{\hspace{10em}}$$

5. In a constant-pressure calorimeter, 65.0 mL of 0.900 M  $\text{H}_2\text{SO}_4$  was added to 65.0 mL of 0.250 M NaOH. The reaction caused the temperature of the solution to rise from 23.60 °C to 25.30 °C.

a) (1 pt) Write a balanced molecular equation (including phases) for the neutralization.

b) (4 pts) If the solution has the same density and specific heat as water, what is  $\Delta H$  for this reaction (per mole of  $\text{H}_2\text{O}$  produced)? You may assume that the total volume is the sum of the individual volumes.

$\Delta H^\circ =$  \_\_\_\_\_

Question	Points Possible	Points Earned	TA Initial
1	5		
2	10		
3	7		
4	8		
5	5		
<b>TOTAL</b>	<b>35</b>		

**LAST NAME:** \_\_\_\_\_

**FIRST NAME:** \_\_\_\_\_

**Student Number:** \_\_\_\_\_

# **CHM 1311 Midterm #2 Fall 2018**

## **STAGE 1 – 60 min**

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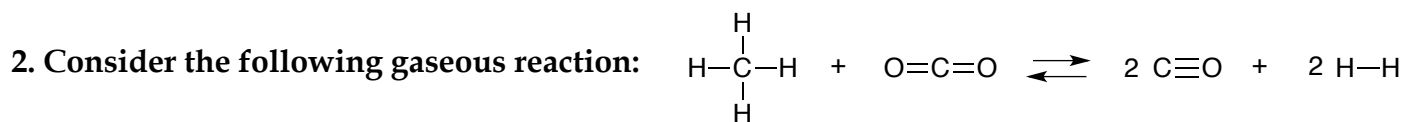
## 1. Short Answer Questions

- a. (0.5 pt) Bond making is always an exothermic process. TRUE FALSE
- b. (1 pt) For the reaction  $A(g) \rightarrow 2B(g)$ , we observe that the rate of disappearance of A is constant as the reaction progresses. Therefore, for the reaction:
- the graph of \_\_\_\_\_ versus time will be a linear plot
  - the half-life will INCREASE DECREASE as  $[A]_0$  increases
- c. (0.5 pt) A chemical equilibrium can be considered to be "going to completion" when the value of K is at least  $10^{-10}$   $10^{-5}$  10  $10^5$  or greater.
- d. (0.5 pt) A buffer made from HA ( $pK_a = 4.82$ ) and NaA has a pH of 4.95. The buffer therefore contains:  $[HA] > [A^-]$   $[HA] < [A^-]$   $[HA] = [A^-]$
- e. (1 pt) In the reaction:  $N_2O_4(g) \rightleftharpoons 2NO_2(g)$  ( $\Delta H = 57.2 \text{ kJ/mol}$ ), the reactant is a colourless gas and the product is a brown gas. A flask contains a mixture of these gases at equilibrium. In the box, write the equilibrium constant and choose the best means which would lead to an increase in the observed colour.
- remove  $NO_2$  and remove heat
- add  $NO_2$  and decrease volume
- remove  $N_2O_4$  and add heat
- add  $N_2O_4$  and increase volume
- K =
- f. (0.5 pt) For the compounds listed below, how many will be *less* soluble in a pH = 4.5 buffer than in pure water? NONE 1 2 3 ALL OF THEM
- |     |          |         |            |
|-----|----------|---------|------------|
| PbS | $CaCO_3$ | $BaF_2$ | $Zn(OH)_2$ |
|-----|----------|---------|------------|
- g. (1 pt) Benzoic acid is titrated with sodium hydroxide. At the HALF equivalence point, pH = \_\_\_\_\_ (*give the value*); at the equivalence point, the pH will be (*circle one*):
- ACIDIC NEUTRAL BASIC IMPOSSIBLE TO PREDICT

## BONUS:

Give the expected products of the following acid-base reaction, label the acid, base, conjugate acid, and conjugate base, and determine the preferred direction of the equilibrium.





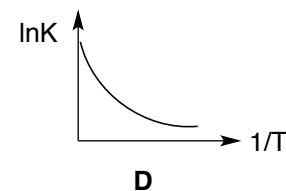
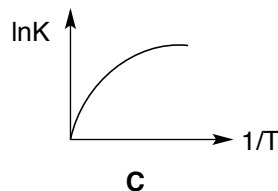
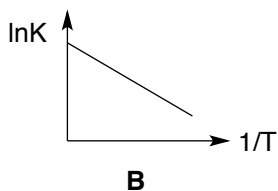
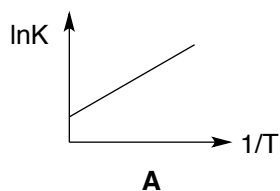
An equimolar mixture of  $\text{CH}_4$  and  $\text{CO}_2$ , with a total pressure of 20.0 bar, are placed in a 1.00 L flask and allowed to equilibrate at 1200 K. At equilibrium, the flask is found to contain 19.6 bar of hydrogen.

a) (4 pts) What is the value of K for the reaction?

b) (3 pts) Using the table of bond energies, estimate the energy change of the reaction.

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C-C	348	H-H	436
C=C	612	O-H	463
C-O	360	O=O	494
C=O	743	H-Br	363
C $\equiv$ O	1070	C-H	412

c) (1 pt) Which of the following would be the correct van't Hoff plot for the reaction?



3. A student mixes 31.0 mL of 2.74 M  $\text{Pb}(\text{NO}_3)_2$  (aq) with 20.0 mL of 0.00163 M  $\text{NaI}$  (aq).

- a) (1 pt) Identify the expected precipitate: \_\_\_\_\_
- b) (8 pts) What are the values of  $[\text{Pb}^{2+}]$ ,  $[\text{Na}^+]$ ,  $[\text{NO}_3^-]$  and  $[\text{I}^-]$  after the solution has reached equilibrium at 25°C? You may assume volumes are additive.

$[\text{Pb}^{2+}] =$  \_\_\_\_\_

$[\text{Na}^+] =$  \_\_\_\_\_

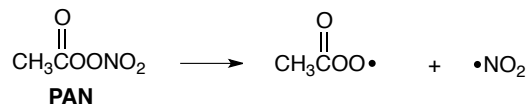
$[\text{NO}_3^-] =$  \_\_\_\_\_

$[\text{I}^-] =$  \_\_\_\_\_

- c) (3 pts) What mass (in mg) of solid precipitate is obtained?

Answer: \_\_\_\_\_

3. Peroxyacetyl nitrate (PAN) is an air pollutant produced during photochemical smog events. PAN is unstable and dissociates into peroxyacetyl radicals and nitrogen dioxide.



- a) (3 pts) Using the data in the table below, derive a rate law for the decomposition of PAN at 25.0°C, as well as the value of the rate constant (with appropriate units).

Trial	Initial [PAN] (M)	Initial Rate (M/min)
1	$8.30 \times 10^{-10}$	$1.92 \times 10^{-11}$
2	$1.66 \times 10^{-9}$	$3.84 \times 10^{-11}$
3	$2.49 \times 10^{-9}$	$5.78 \times 10^{-11}$

Rate law is: \_\_\_\_\_

Rate constant is: \_\_\_\_\_

- b) (2 pts) The decomposition of PAN has a half-life of 35.0 hr at 0.00°C. What is the rate constant for this reaction at this temperature? Use the same units as part (a).

Answer: \_\_\_\_\_

5. (5 pts) After a vacation of scuba-diving, Dr. Fox has to clean and rinse all her scuba gear before putting it back into storage. She wants to use "*Diver's Buddy Scuba Shampoo*", a commercially available aqueous solution of trimethylamine ( $\text{N}(\text{CH}_3)_3$ ,  $K_b = 6.31 \times 10^{-6}$ ). Dr. Fox measures the pH of the solution and finds it to be 10.55. What is the concentration of trimethylamine in the shampoo, in mol/L?

Answer: \_\_\_\_\_

Question	Points Possible	Points Earned	TA Initial
1	5		
2	8		
3	12		
4	5		
5	5		
<b>TOTAL</b>	<b>35</b>		

**LAST name (IN CAPITAL LETTERS):** \_\_\_\_\_

**FIRST name:** \_\_\_\_\_

**Student Number:** \_\_\_\_\_

**Seat Number:** \_\_\_\_\_

**Please INITIAL HERE when you have verified that there are 17 pages in your exam copy:**

# **CHM 1311 Final Exam December 2018**

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

**There are 17 pages in this exam. A periodic table, data tables, and a formula sheet are provided at the end. You may remove these pages off of the exam and use them to cover your work. Please show all work to receive partial credit. You have 180 minutes to complete the exam.**

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<b>Question</b>	<b>Points Possible</b>	<b>Points Earned</b>	<b>TA Initial</b>
1	20		
2	10		
3	10		
4	10		
5	10		
6	10		
7	10		
8	10		
9	10		
<b>TOTAL</b>	<b>100</b>		

## 1. Short Answer Questions.

a) (0.5 pt) 1.0 mol of an ideal gas is placed in a 1.0 L flask at 22°C. Which of the following would result in the greatest increase in the pressure of the gas?

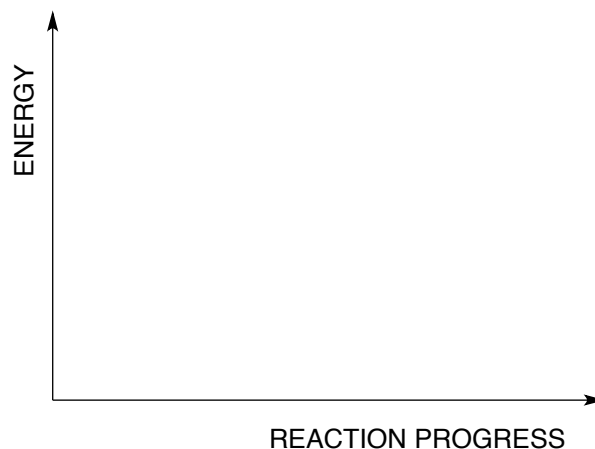
- reducing the volume of the container to 0.50 L
- increasing the amount of gas to 1.5 mol
- increasing the temperature to 300°C

b) (1.5 pts) For an endothermic contraction of a gas:

- |                              |          |          |         |
|------------------------------|----------|----------|---------|
| • The value of W is          | POSITIVE | NEGATIVE | UNKNOWN |
| • The value of q is          | POSITIVE | NEGATIVE | UNKNOWN |
| • The value of $\Delta U$ is | POSITIVE | NEGATIVE | UNKNOWN |

c) (3 pts) On the axes provided at right, draw a line (or curve) representing the reaction profile for a reaction  $A \rightarrow C$  with the following characteristics:

- a two-step mechanism,  $A \rightarrow B$ , then  $B \rightarrow C$
- $E_a$  of step 2 = 50 kJ/mol
- step 1 is two times slower than step 2
- $\Delta H = -80$  kJ/mol



On your profile, label the following: A, B, C,  $E_{a1}$  (for step 1),  $E_{a2}$  (for step 2), and  $\Delta H$ .

d) (0.5 pt) Below is a hypothetical configuration for the ground state of a scandium atom.

This configuration is incorrect because:  $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{14} s^2$

- it contains one or more orbitals that do not exist
- it contains too few electrons
- it contains too many electrons
- it contains electrons in incorrect orbitals
- it contains orbitals listed in incorrect order

e) (1 pt) The number of atoms in 10.0 g of  $\text{CaCO}_3$  (100.0 g/mol) is:

1.81 x 10<sup>23</sup>

6.02 x 10<sup>22</sup>

3.01 x 10<sup>23</sup>

1.21 x 10<sup>23</sup>

- f) (1 pt) The cheese on a pizza stays hot for a long time, while the crust cools down more quickly, making it possible for you to hold the pizza slice, yet still burn your mouth on the cheese. Which substance has the smaller specific heat capacity?

CRUST

CHEESE

- g) (2.5 pt) Phosphorous acid has  $pK_{a1} = 1.30$  and  $pK_{a2} = 6.70$ . An aqueous solution of this acid is titrated with NaOH (aq). At the *first* equivalence point, the pH of the solution will be

ACIDIC

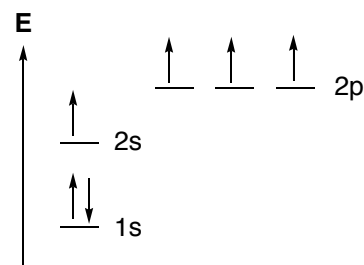
BASIC

NEUTRAL

Write the equation for the expected hydrolysis:

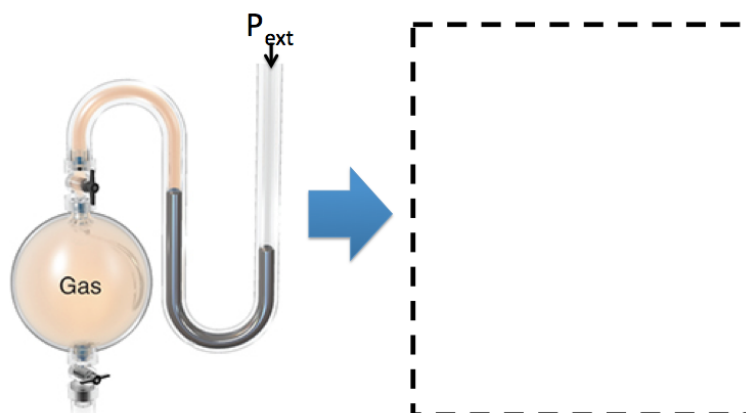
- h) (0.5 pt) A student draws the orbital energy diagram at right for a carbon atom. As shown, this diagram:

- is correct  
 disobeys the Pauli Exclusion Principle  
 disobeys Hund's Rule  
 disobeys the Aufbau Principle



- i) (2 pts) For a first order reaction, the half-life \_\_\_\_\_ with increasing reactant concentration. For a second order reaction, the half-life \_\_\_\_\_ with increasing reactant concentration.

- j) (1 pt) 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.



k) (1 pt) Solid potassium chromate is slowly added to an aqueous solution that contains 0.200 M each  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  ions. The compound that precipitates first is: \_\_\_\_\_.

l) (2 pts) Give the maximum number of electrons that can have the following quantum numbers:

•  $n = 2$  and  $l = 1$                       number of electrons = \_\_\_\_\_

•  $n = 5$ ,  $l = 5$  and  $m_l = 0$                       number of electrons = \_\_\_\_\_

m) (1 pt) A one litre balloon is filled with neon gas. A hole is made in the balloon and the gas effuses at a rate of 0.0280 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of effusion would be \_\_\_\_\_.

n) (0.5 pt) It is possible to prepare a buffer by taking a strong base and titrating it with a strong acid to the half equivalence point.      TRUE      FALSE

o) (1 pt) For an ideal gas, a graph of PV versus T will be a linear relationship with a slope that is directly proportional to the gas's:

KINETIC ENERGY

MOLAR MASS

ENTHALPY

MASS

p) (1 pt) Decreasing the temperature of an exothermic reaction will:

- increase the yield and the rate
- increase the yield and decrease the rate
- decrease the yield and increase the rate
- decrease the yield and rate

### BONUS

Complete the following sentence: "Chemists aren't \_\_\_\_\_,

we're \_\_\_\_\_!"

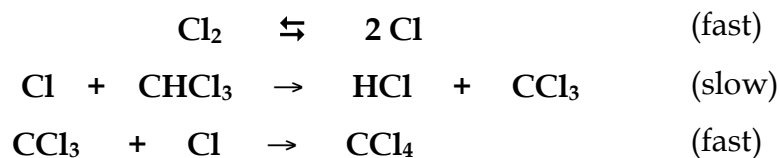
2. You wish to prepare a buffer solution with  $\text{pH} = 9.45$ .
- a) How many grams of  $(\text{NH}_4)_2\text{SO}_4$  would you add to 425 mL of 0.258 M  $\text{NH}_3$  to do this? You may assume that the solution's volume remains constant.  $K_b$  of  $\text{NH}_3 = 1.8 \times 10^{-5}$

Answer: \_\_\_\_\_

- b) You have access to additional 0.258 M  $\text{NH}_3$  and more solid  $(\text{NH}_4)_2\text{SO}_4$ . Which buffer component, and how much (in g or mL) would you add to 0.100 L of the buffer in part (a) to change its pH to 9.30? You may assume that the solution's volume remains constant.

Component: \_\_\_\_\_ Amount: \_\_\_\_\_

3. Consider the following three-step mechanism:



- a) (2 pts) What is the overall reaction? Identify any reaction intermediates.
- b) (3 pts) The rate law is determined experimentally to be:  $\text{rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$ . Is the proposed mechanism valid? Why or why not?
- c) (2 pts) When  $[\text{CHCl}_3]_i = 1.05 \times 10^{-4} \text{ M}$  and  $[\text{Cl}_2]_i = 2.64 \text{ M}$ , the initial rate of reaction is  $2.4 \times 10^{-3} \text{ M/s}$ . Find the value of the rate constant, with the appropriate units.
- d) (3 pts) What will be  $[\text{CHCl}_3]$  after 12.0 s using the conditions from part c)? HINT: note the relative reactant concentrations!

**4. Electrons in Atoms.**

a) (4 pts) Draw a diagram of Bohr's model of the hydrogen atom showing the transition of an electron from the  $n = 5$  level to the ground state. What is the change in energy (in kJ/mol) of this transition?

b) (3 pts) Calculate the wavelength (in nm) that corresponds to the energy found in part a).

c) (4 pts) Between Cr and Cr<sup>+</sup>, which species is expected to be paramagnetic? Circle your answer below. To obtain full marks, draw the orbital energy diagram for each species.

Cr

Cr<sup>+</sup>

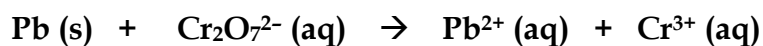
NEITHER

BOTH

5. The age of rocks is sometimes calculated from the measured excess of lead-206 atoms over the normal abundance. Lead-206 has a natural abundance of 23.6%.
- a) (1 pt) Write the atomic symbol for lead-206 in the form  ${}^A_ZX$ : \_\_\_\_\_
- b) (5 pts) What volume block of lead (in  $\text{cm}^3$ ) will contain  $8.34 \times 10^{21}$  atoms of lead-206? The density of lead is  $11.35 \text{ g/cm}^3$ .

Answer: \_\_\_\_\_

- c) (4 pts) The lead atoms can be extracted from pulverized rock dust via the aqueous redox reaction shown below. Balance the equation, under acidic conditions (including phases).



6. Methanol,  $\text{CH}_3\text{OH}$ , is synthesized directly on the industrial scale by the reaction of carbon monoxide with hydrogen gas.

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

b) (3 pts) Using the data below, what is the value for the enthalpy change of the reaction of part (a) at  $25^\circ\text{C}$ ?

	$\Delta H_f^\circ$ (kJ/mol)
$\text{CO(g)}$	-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: \_\_\_\_\_

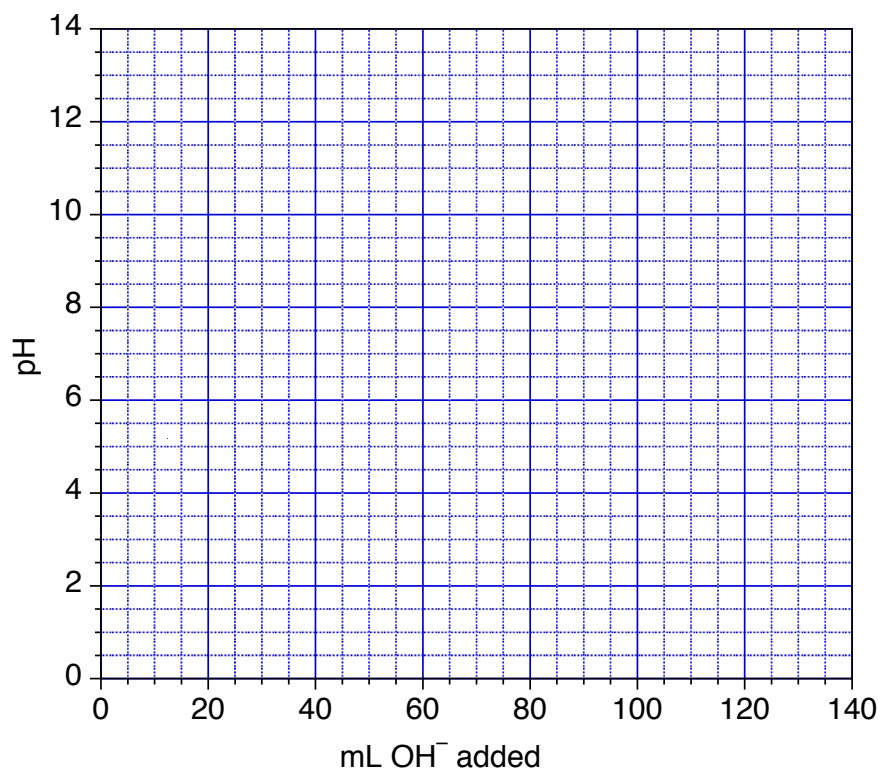
c) (4 pts) The value of the equilibrium constant for the above reaction at 298 K is  $2.27 \times 10^4$ . Calculate the value of the equilibrium constant at 500 K.

Answer: \_\_\_\_\_

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

7. You are performing a titration of 80.0 mL of 0.0900 M HCN with 0.0900 M NaOH. Determine the pH of the solution:

- (3 pts) initially
- (2 pts) at the half-equivalence point
- (4 pts) at the equivalence point
- (1 pt) Use these values to sketch a titration curve on the graph provided.



8. A student mixes 40.0 mL of 0.0122 M  $\text{Pb}(\text{NO}_3)_2$  (aq) with 40.0 mL of 1.76 M  $\text{KCl}$  (aq).

- a) (1 pt) Identify the expected precipitate: \_\_\_\_\_
- b) (8 pts) What are the values of  $[\text{Pb}^{2+}]$ ,  $[\text{K}^+]$ ,  $[\text{NO}_3^-]$  and  $[\text{Cl}^-]$  after the solution has reached equilibrium at 25°C? You may assume volumes are additive.

$[\text{Pb}^{2+}] =$  \_\_\_\_\_

$[\text{K}^+] =$  \_\_\_\_\_

$[\text{NO}_3^-] =$  \_\_\_\_\_

$[\text{Cl}^-] =$  \_\_\_\_\_

- c) (3 pts) What mass (in mg) of solid precipitate is obtained?

Answer: \_\_\_\_\_

9. In the Haber synthesis of ammonia,  $\text{N}_2$  and  $\text{H}_2$  react at high temperature to produce  $\text{NH}_3$ .
- a) (6 pts) In a typical reaction, 45.0 kg of  $\text{H}_2$  and 160.0 kg of  $\text{N}_2$  react to produce 152 kg of  $\text{NH}_3$ . Find the percent yield of the reaction, and the mass of *unreacted*  $\text{N}_2$  (in kg).

Percent Yield = \_\_\_\_\_      Mass of  $\text{N}_2$  = \_\_\_\_\_

- b) (4 pts) One of the major industrial products of ammonia is urea,  $\text{NH}_2\text{CONH}_2$ . Calculate the molarity of a 1.70 mol/kg aqueous solution of urea. The density of the solution is 1.2 g/mL.

Molality = \_\_\_\_\_

CHM1311 E

Name : \_\_\_\_\_

TWO STAGE DGD QUIZ

October 2018

## STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. (6 pts) Hydrogen fluoride is produced industrially by the action of sulphuric acid on  $\text{CaF}_2$ . If 365 kg of  $\text{CaF}_2$  is treated with excess sulphuric acid and 155 kg of HF is produced, what is the percent yield and what mass (in kg) of  $\text{CaF}_2$  remains unreacted? The other product of the reaction is  $\text{CaSO}_4$ .

Using the available data and a balanced chemical equation, we can use molar masses to find the number of moles of the reactant and the obtained product:

	$\text{H}_2\text{SO}_4 + \text{CaF}_2 \rightarrow 2 \text{HF} + \text{CaSO}_4$			
mass (g)	excess	365 000	155 000	
molar mass (g/mol)		78.08	20.00	
moles		4675	7750	

First, we find the theoretical number of moles of product possible:

$$? \text{ theo. mol HF from CaF}_2 = 4675 \text{ mol CaF}_2 \times \frac{2 \text{ mol HF}}{1 \text{ mol CaF}_2} = 9350 \text{ mol}$$

With the theoretical and actual yields of HF, we can find the percent yield:

$$? \% \text{ yield HF} = \frac{7750 \text{ mol}}{9350 \text{ mol}} \times 100\% = 83\%$$

Since the yield is NOT 100%, we know that NOT ALL OF THE  $\text{CaF}_2$  REACTS. Using the actual amount of HF formed, we can work backwards to find the amount of  $\text{CaF}_2$  that actually reacted, and then the amount of unreacted  $\text{CaF}_2$ :

$$? \text{ mol CaF}_2 \text{ reacted} = 7750 \text{ mol HF} \times \frac{1 \text{ mol CaF}_2}{2 \text{ mol HF}} = 3875 \text{ mol}$$

$$? \text{ kg CaF}_2 \text{ leftover} = (4675 \text{ mol} - 3875 \text{ mol}) \times \frac{78.08 \text{ g CaF}_2}{1 \text{ mol CaF}_2} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 62.5 \text{ kg}$$

Percent Yield = 83%      Mass of  $\text{CaF}_2$  = 62.5 kg

2. (6 pts) Shoppers Drug Mart sells a homeopathic cough syrup (100 mL bottle for about \$8) that contains arsenic at a concentration of "14 CH". This corresponds to a ratio of 1.00 g of arsenic to  $10^{28}$  g of syrup. How many bottles of this cough syrup must you drink in order to consume one atom of arsenic? The cough syrup has a density of 2.45 g/mL.

THIS QUESTION IS A MODIFIED IN-CLASS ECHO360 PROBLEM

$$\begin{aligned} \frac{? \text{ atoms As}}{\text{L syrup}} &= \frac{1.00 \text{ g As}}{10^{28} \text{ g syrup}} \times \frac{\text{mol As}}{74.92 \text{ g As}} \times \frac{6.022 \times 10^{23} \text{ atoms As}}{\text{mol As}} \times \frac{2.45 \text{ g syrup}}{\text{mL syrup}} \times \frac{1000 \text{ mL syrup}}{\text{L syrup}} \\ &= 0.00197 \text{ atoms As/L} \\ ? \text{ bottles} &= 1 \text{ atom As} \times \frac{1 \text{ L}}{0.00197 \text{ atoms As}} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{1 \text{ bottle}}{100 \text{ mL}} \\ &= 5078 \text{ bottles (5080 bottles, with sig figs)} \end{aligned}$$

Number of bottles = \_\_\_\_\_

3. (3 pts) Walmart sells antifreeze, an aqueous solution that is 28.6% ethylene glycol ( $\text{C}_2\text{H}_6\text{O}_2$ ) by mass. If the density of this solution is 1.03 g/cm<sup>3</sup>, calculate its molality.

THIS QUESTION WAS COVERED IN DGD 2 (YOU CAN WATCH THE VIDEO)

28.6% by mass means there are 28.6 g  $\text{C}_2\text{H}_6\text{O}_2$  in 100 g of solution. Therefore, the mass of water in the solution is the difference between these two values:

	$\text{C}_2\text{H}_6\text{O}_2$	$\text{H}_2\text{O}$	SOLUTION
mass (g)	28.6	71.4	100
molar mass (g/mol)	62.07		
mol	0.461		

$$\therefore \text{molality} = ? \frac{\text{mol C}_2\text{H}_6\text{O}_2}{\text{kg H}_2\text{O}} = \frac{0.461 \text{ mol}}{71.4 \text{ g H}_2\text{O}} \times \frac{1000 \text{ g}}{\text{kg}} = 6.5 \text{ mol/kg}$$

Molality = \_\_\_\_\_

## 1. Short Answer Questions

- a) (1 pt) Four balloons are filled to the same volume with the following gases and a small hole is made in each balloon. Circle the one that will deflate the *fastest* and underline the one that will deflate the *slowest*.



- b) (1.5 pts) The standard heat of formation of solid potassium permanganate is -813.4 kJ. Write the chemical equation for the reaction to which this value applies.



- c) (0.5 pt) Which of the following is/are a state function?      q      W       $\Delta U$        $\Delta H$
- d) (1 pt) Starting with an atom of germanium-72, we add 3 protons, add 6 neutrons, and add 4 electrons to the atom. Fill in the blanks for our new species:

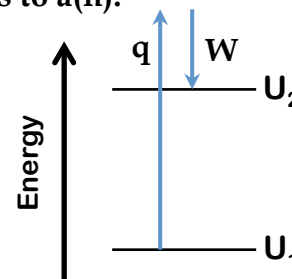
Number of protons	Number of neutrons	Number of electrons	Chemical Symbol
35	46	36	${}_{35}^{81}\text{Br}^-$

- e) (0.5 pt) A sample of a gas is slowly expanded from 4.0 L to 8.0 L. In order for the average kinetic energy of the gas to increase, the gas must also be simultaneously heated.

TRUE      FALSE

- f) (0.5 pt) The energy change shown in the diagram at right corresponds to a(n):

- EXOTHERMIC CONTRACTION  
 ENDOTHERMIC CONTRACTION  
 EXOTHERMIC EXPANSION  
 ENDOTHERMIC EXPANSION



(1 pt) BONUS:

In order to convert an empirical formula to a molecular formula, one must know/determine the \_\_\_\_\_ **MOLAR/MOLECULAR MASS** \_\_\_\_\_ of the unknown compound.

2. Ethanol ( $\text{CH}_3\text{CH}_2\text{OH}$ ) is used to make other organic compounds. In concentrated sulphuric acid, ethanol forms diethyl ether and water:



In a side reaction, some ethanol forms ethylene and water:



THIS QUESTION IS SILBERBERG 3.182 AND WAS COVERED IN DGD #2

a) (4 pts) If 50.0 g of ethanol yields 35.9 g of diethyl ether, what is the percent yield of diethyl ether?

Let Et =  $\text{CH}_3\text{CH}_2$

$$\begin{aligned} ? \text{ g Et}_2\text{O (theoretical)} &= 50.0 \text{ g EtOH} \times \frac{\text{mol EtOH}}{46.07 \text{ g EtOH}} \times \frac{1 \text{ mol Et}_2\text{O}}{2 \text{ mol EtOH}} \times \frac{74.12 \text{ g Et}_2\text{O}}{\text{mol Et}_2\text{O}} \\ &= 40.2 \text{ g} \\ \% \text{ yield} &= \frac{35.9 \text{ g}}{40.2 \text{ g}} \times 100\% \\ &= 89.3\% \end{aligned}$$

%Yield = \_\_\_\_\_

b) (4 pts) If 45.0% of the ethanol that did not produce the ether reacts by the side reaction, what mass (in g) of ethylene is produced?

? g EtOH unreacted =  $40.2 \text{ g} - 35.9 \text{ g} = 4.3 \text{ g}$

$$\begin{aligned} ? \text{ mol EtOH unreacted} &= 4.3 \text{ g Et}_2\text{O} \times \frac{\text{mol Et}_2\text{O}}{74.12 \text{ g Et}_2\text{O}} \times \frac{2 \text{ mol EtOH}}{1 \text{ mol Et}_2\text{O}} \\ &= 0.116 \text{ mol} \end{aligned}$$

$$\begin{aligned} ? \text{ g CH}_2\text{CH}_2 &= 0.116 \text{ mol EtOH unr'd} \times \frac{45.0 \text{ mol EtOH side rxn}}{100 \text{ mol EtOH unr'd}} \times \frac{1 \text{ mol CH}_2\text{CH}_2}{1 \text{ mol EtOH}} \times \frac{28.05 \text{ g}}{\text{mol CH}_2\text{CH}_2} \\ &= 1.46 \text{ g} \end{aligned}$$

Mass = \_\_\_\_\_

c) (2 pts) What volume (in L) does the ethylene gas (produced in part b) occupy at STP?

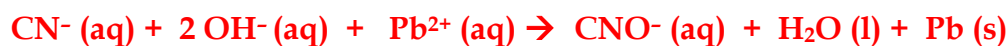
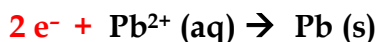
$$\begin{aligned} ? \text{ L} &= 1.46 \text{ g} \times \frac{\text{mol}}{28.05 \text{ g}} \times \frac{0.083145 \text{ L} \cdot \text{bar}}{\text{mol} \cdot \text{K}} \times \frac{273.15 \text{ K}}{1.00 \text{ bar}} \\ &= 1.18 \text{ L} \end{aligned}$$

Volume = \_\_\_\_\_

3. A salesman comes to your door and tells you that the tap water in your neighbourhood has recently been tested and high levels of lead (Pb) have been found. He can sell you a purification device for \$7500 that can attach to your tap and remove the lead ions from the water. He wants to test your water to see if it is needed; all he needs from you is a small sample of tap water (100.0 mL).

**THIS IS A NEW QUESTION**

- a) (3 pts) His test kit uses the following half reactions to test for the lead ions. Find the overall balanced redox reaction, under basic conditions (including phases).



↑  
RED AGENT

↑  
OX AGENT

- b) (1 pt) Identify the oxidizing agent and the reducing agent in your reaction above.
- c) (2 pts) The salesman tests 100.0 mL of your tap water, gasps, and finds that your glass of water contains 9 billion Pb ions in it ( $9.00 \times 10^9$ ) and encourages you to buy the purification device. According to his test results, what would be the mass (in mg) of lead in 1.00 L of water?

$$\begin{aligned} ? \text{ mg} &= 1 \text{ L} \times \frac{1000 \text{ mL}}{1 \text{ L}} \times \frac{9.00 \times 10^9 \text{ ions}}{100 \text{ mL}} \times \frac{\text{mol}}{6.022 \times 10^{23} \text{ ions}} \times \frac{207.2 \text{ g Pb}}{\text{mol}} \times \frac{1000 \text{ mg}}{1 \text{ g}} \\ &= 3.1 \times 10^{-8} \text{ mg Pb} \end{aligned}$$

Mass = \_\_\_\_\_

- d) (1 pt) Health Canada says that concentrations of 0.01 ppm (or 0.01 mg/L) and lower are safe. Do you spend \$7500 on the purification system?

**Based on the result from part c, the actual concentration ( $3.1 \times 10^{-8}$  mg/L) is nearly 1 million times LOWER than the recommended level. So, HECK NO!**

4. In class, Dr. Fox showed video of scuba diving in False Bay, South Africa, where the water temperature was a chilly 13.5°C. Despite wearing two 5 mm thick neoprene wetsuits, Dr. Fox still lost body heat at a rate of 38.0 J per second.

**THIS QUESTION IS FROM THE 2014 MIDTERM 1**

a) (2 pts) How much body heat, in kJ, was lost over the course of a 45.0 min dive?

$$? \text{ kJ} = 45.0 \text{ min} \times \frac{60 \text{ s}}{1 \text{ min}} \times \frac{38.0 \text{ J}}{\text{s}} \times \frac{1 \text{ kJ}}{1000 \text{ J}} = 102.6 \text{ kJ}$$

Technically, the sign here would be negative (to show heat leaving the system), but since this is already acknowledged in the question, it's not necessary.

$$q = \underline{\hspace{10em}}$$

b) (3 pts) To recuperate this energy loss, Dr. Fox decides to eat a candy bar, which contains glucose, C<sub>6</sub>H<sub>12</sub>O<sub>6</sub>. Using the data table, determine the enthalpy of combustion of glucose, in kJ/mol.

Substance	$\Delta H_f^\circ$ (kJ/mol)
CO (g)	-110.5
CO <sub>2</sub> (g)	-393.5
O <sub>3</sub> (g)	143
CH <sub>3</sub> OH (l)	-238.6
C <sub>2</sub> H <sub>5</sub> OH (l)	-277.6
C <sub>6</sub> H <sub>12</sub> O <sub>6</sub> (s)	-1273.3
C <sub>12</sub> H <sub>22</sub> O <sub>11</sub> (s)	-2221.7
H <sub>2</sub> O (l)	-285.8



$$\begin{aligned} \Delta H^\circ_{\text{comb}} &= \{(6 \times \Delta H^\circ_f \text{CO}_2) + (6 \times \Delta H^\circ_f \text{H}_2\text{O})\} - \{(1 \times \Delta H^\circ_f \text{C}_6\text{H}_{12}\text{O}_6) + (6 \times \Delta H^\circ_f \text{O}_2)\} \\ &= \{(6 \times -393.5) + (6 \times -285.8)\} - \{(1 \times -1273.3) + (6 \times 0)\} \\ &= -2802.5 \text{ kJ/mol} \end{aligned}$$

$$\Delta H^\circ_{\text{comb}} = \underline{\hspace{10em}}$$

c) (3 pts) If the candy bar contains 8.55% glucose by mass, how many grams of it will Dr. Fox need to eat to balance out the heat lost in part (a)?

$$\begin{aligned} ? \text{ g candy} &= 102.6 \text{ kJ} \times \frac{\text{mol C}_6\text{H}_{12}\text{O}_6}{2802.5 \text{ kJ}} \times \frac{180 \text{ g C}_6\text{H}_{12}\text{O}_6}{\text{mol C}_6\text{H}_{12}\text{O}_6} \times \frac{100 \text{ g candy}}{8.55 \text{ g C}_6\text{H}_{12}\text{O}_6} \\ &= 77.1 \text{ g candy} \end{aligned}$$

$$\text{Mass} = \underline{\hspace{10em}}$$

5. In a constant-pressure calorimeter, 65.0 mL of 0.900 M  $\text{H}_2\text{SO}_4$  was added to 65.0 mL of 0.250 M NaOH. The reaction caused the temperature of the solution to rise from 23.60 °C to 25.30 °C.

**THIS QUESTION IS FROM THE 2017 MIDTERM 1**

a) (1 pt) Write a balanced molecular equation (including phases) for the neutralization.



b) (4 pts) If the solution has the same density and specific heat as water, what is  $\Delta H$  for this reaction (per mole of  $\text{H}_2\text{O}$  produced)? You may assume that the total volume is the sum of the individual volumes.

$$? \text{ mol H}_2\text{O from H}_2\text{SO}_4 = 0.065 \text{ L soln} \times \frac{0.900 \text{ mol H}_2\text{SO}_4}{\text{L soln}} \times \frac{2 \text{ mol H}_2\text{O}}{1 \text{ mol H}_2\text{SO}_4} = 0.117 \text{ mol}$$

$$? \text{ mol H}_2\text{O from NaOH} = 0.065 \text{ L soln} \times \frac{0.250 \text{ mol NaOH}}{\text{L soln}} \times \frac{2 \text{ mol H}_2\text{O}}{2 \text{ mol NaOH}} = 0.01625 \text{ mol}$$

**Therefore, the NaOH is the limiting reagent.**

$$\begin{aligned} q_{\text{reaction}} &= -q_{\text{surr}} \\ &= -m_{\text{total}} \times c \times \Delta T \\ &= -(130 \text{ g} \times \frac{1 \text{ mL}}{1 \text{ g}})(4.184 \text{ J/g}^\circ\text{C})(25.30^\circ\text{C} - 23.60^\circ\text{C}) \\ &= -924.7 \text{ J} \\ \Delta H &= \frac{q}{n} = \frac{-924.7 \text{ J}}{0.01625 \text{ mol}} = -56.9 \text{ kJ/mol} \end{aligned}$$

$\Delta H^\circ =$  \_\_\_\_\_

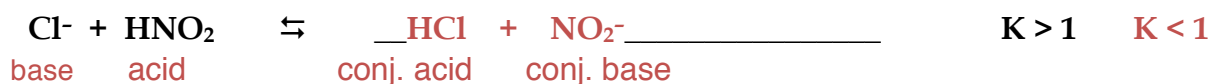
## 1. Short Answer Questions

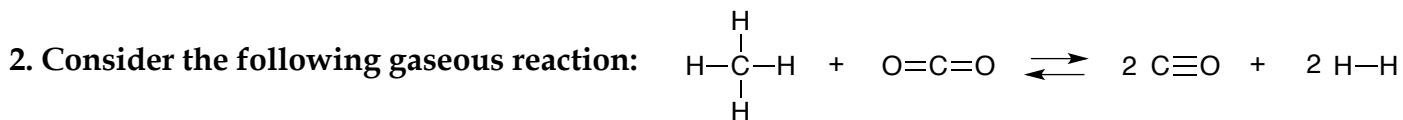
- a. (0.5 pt) Bond making is always an exothermic process. **TRUE** FALSE
- b. (1 pt) For the reaction  $A(g) \rightarrow 2 B(g)$ , we observe that the rate of disappearance of A is constant as the reaction progresses. Therefore, for the reaction:
- the graph of   [A]   versus time will be a linear plot
  - the half-life will **INCREASE** DECREASE as  $[A]_0$  increases
- c. (0.5 pt) A chemical equilibrium can be considered to be "going to completion" when the value of K is at least  $10^{-10}$   $10^{-5}$  10  **$10^5$**  or greater.
- d. (0.5 pt) A buffer made from HA ( $pK_a = 4.82$ ) and NaA has a pH of 4.95. The buffer therefore contains:  $[HA] > [A^-]$   **$[HA] < [A^-]$**   $[HA] = [A^-]$
- e. (1 pt) In the reaction:  $N_2O_4(g) \rightleftharpoons 2 NO_2(g)$  ( $\Delta H = 57.2 \text{ kJ/mol}$ ), the reactant is a colourless gas and the product is a brown gas. A flask contains a mixture of these gases at equilibrium. In the box, write the equilibrium constant and choose the best means which would lead to an increase in the observed colour.
- remove  $NO_2$  and remove heat  
 add  $NO_2$  and decrease volume  
 remove  $N_2O_4$  and add heat  
 **add  $N_2O_4$  and increase volume**

$$K = \frac{P_{NO_2}^2}{P_{N_2O_4}}$$
- f. (0.5 pt) For the compounds listed below, how many will be *less* soluble in a pH = 4.5 buffer than in pure water? **NONE** 1 2 3 ALL OF THEM
- |     |                   |                  |                     |
|-----|-------------------|------------------|---------------------|
| PbS | CaCO <sub>3</sub> | BaF <sub>2</sub> | Zn(OH) <sub>2</sub> |
|-----|-------------------|------------------|---------------------|
- g. (1 pt) Benzoic acid is titrated with sodium hydroxide. At the HALF equivalence point, pH = **4.20** (give the value); at the equivalence point, the pH will be (circle one):
- ACIDIC NEUTRAL **BASIC** IMPOSSIBLE TO PREDICT

## BONUS:

Give the expected products of the following acid-base reaction, label the acid, base, conjugate acid, and conjugate base, and determine the preferred direction of the equilibrium.





An equimolar mixture of  $\text{CH}_4$  and  $\text{CO}_2$ , with a total pressure of 20.0 bar, are placed in a 1.00 L flask and allowed to equilibrate at 1200 K. At equilibrium, the flask is found to contain 19.6 bar of hydrogen.

THIS IS A SLIGHTLY MODIFIED VERSION OF SILBERBERG SUGGESTED PROBLEM 15.97

a) (4 pts) What is the value of K for the reaction?

$P_{\text{total}} = 20.0 \text{ bar} = P_{\text{CH}_4} + P_{\text{CO}_2}$ . Since  $n_{\text{CH}_4} = n_{\text{CO}_2}$  (EQUIMOLAR), that means each gas has an initial partial pressure of 10.0 bar.

	$\text{CH}_4(\text{g})$	$+$	$\text{CO}_2(\text{g})$	$\rightleftharpoons$	$2 \text{CO}(\text{g})$	$+$	$2 \text{H}_2(\text{g})$
I	10.0		10.0		0		0
C	$-x$		$-x$		$+2x$		$+2x$
	-9.8		-9.8		+19.6		+19.6
E	0.246		0.2		19.6		19.6

$$K_P = \frac{(P_{\text{CO}})^2 \times (P_{\text{H}_2})^2}{P_{\text{CH}_4} \times P_{\text{CO}_2}} = \frac{(19.6)^2 (19.6)^2}{(0.2)(0.2)} = 3.7 \times 10^6$$

b) (3 pts) Using the table of bond energies, estimate the energy change of the reaction.

**BROKEN:**

4 x C-H	4 x 412 kJ	1648 kJ
2 x C=O	2 x 743 kJ	1486 kJ
	<b>TOTAL</b>	<b>+ 3134 kJ</b>

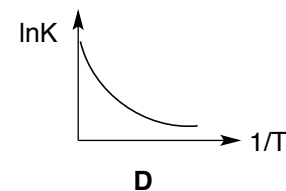
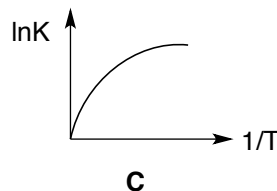
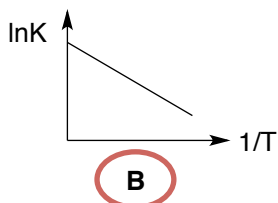
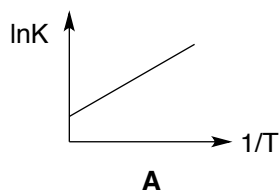
**FORMED:**

2 x C≡O	2 x -1070 kJ	-2140 kJ
2 x H-H	2 x 436 kJ	-872 kJ
	<b>TOTAL</b>	<b>-3012 kJ</b>

Bond	Energy (kJ/mol)	Bond	Energy (kJ/mol)
C-C	348	H-H	436
C=C	612	O-H	463
C-O	360	O=O	494
C=O	743	H-Br	363
C≡O	1070	C-H	412

$$\Delta H \text{ (or } \Delta E) = +3134 \text{ kJ} + (-3012 \text{ kJ}) = +122 \text{ kJ}$$

c) (1 pt) Which of the following would be the correct van't Hoff plot for the reaction?



3. A student mixes 31.0 mL of 2.74 M  $\text{Pb}(\text{NO}_3)_2$  (aq) with 20.0 mL of 0.00163 M  $\text{NaI}$  (aq).

THIS QUESTION IS FROM SAPLING ASSIGNMENT #8 AND WAS COVERED IN DGD#9

- a) (1 pt) Identify the expected precipitate:  $\text{PbI}_2$
- b) (8 pts) What are the values of  $[\text{Pb}^{2+}]$ ,  $[\text{Na}^+]$ ,  $[\text{NO}_3^-]$  and  $[\text{I}^-]$  after the solution has reached equilibrium at 25°C? You may assume volumes are additive.

SINCE MANY STUDENTS HAVE ASKED ME ABOUT THIS PROBLEM, I WILL PRESENT A STEP-BY-STEP SOLUTION HERE. PLEASE NOTE THAT IT IS NOT NECESSARY TO SHOW EVERY SINGLE INDIVIDUAL CALCULATION TO RECEIVE ALL POINTS, THIS IS JUST FOR CLARITY:

First, find the initial moles of each ion:

$$\begin{aligned} ? \text{ mol Pb}^{2+} &= \frac{2.74 \text{ mol Pb}(\text{NO}_3)_2}{\text{L}} \times \frac{1 \text{ mol Pb}^{2+}}{1 \text{ mol Pb}(\text{NO}_3)_2} \times 0.0310 \text{ L} = 8.494 \times 10^{-2} \text{ mol} \\ ? \text{ mol NO}_3^- &= \frac{2.74 \text{ mol Pb}(\text{NO}_3)_2}{\text{L}} \times \frac{2 \text{ mol NO}_3^-}{1 \text{ mol Pb}(\text{NO}_3)_2} \times 0.0310 \text{ L} = 0.1699 \text{ mol} \\ ? \text{ mol Na}^+ &= \frac{0.00163 \text{ mol NaI}}{\text{L}} \times \frac{1 \text{ mol Na}^+}{1 \text{ mol NaI}} \times 0.0200 \text{ L} = 3.26 \times 10^{-5} \text{ mol} \\ ? \text{ mol I}^- &= \frac{0.00163 \text{ mol NaI}}{\text{L}} \times \frac{1 \text{ mol I}^-}{1 \text{ mol NaI}} \times 0.0200 \text{ L} = 3.26 \times 10^{-5} \text{ mol} \end{aligned}$$

Now, treat the precipitation as a limiting-reagent type problem, and precipitate the maximum amount of  $\text{PbI}_2$  possible:

	$\text{Pb}^{2+}$	+	$2 \text{ I}^-$	$\rightarrow$	$\text{PbI}_2$ (s)
B	$8.494 \times 10^{-2}$				0
A			$3.26 \times 10^{-5}$		
M	$- \frac{1}{2} \times (3.26 \times 10^{-5})$		$- 3.26 \times 10^{-5}$		$+ \frac{1}{2} \times (3.26 \times 10^{-5})$
A	$8.492 \times 10^{-2}$		0		$1.63 \times 10^{-5}$

So,  $1.63 \times 10^{-5}$  mol of  $\text{PbI}_2$  precipitates, leaving behind  $8.492 \times 10^{-2}$  mol of excess  $\text{Pb}^{2+}$  ions in solution.

At this point, our total volume is: 31.0 mL + 20.0 mL = 51.0 mL. We can now calculate the new concentrations of aqueous ions AFTER the precipitation (but BEFORE turning on the EQM)  $\rightarrow$

Note:  $\text{Na}^+$  and  $\text{NO}_3^-$  are spectator ions, and thus *their* concentrations are the correct final answers.

$$? [\text{Pb}^{2+}] = \frac{8.494 \times 10^{-2} \text{ mol}}{0.0510 \text{ L}} = 1.665 \text{ M}$$

$$? [\text{NO}_3^-] = \frac{0.1699 \text{ mol}}{0.0510 \text{ L}} = 3.33 \text{ M}$$

$$? [\text{Na}^+] = \frac{3.26 \times 10^{-5} \text{ mol}}{0.0510 \text{ L}} = 6.39 \times 10^{-4} \text{ M}$$

$$? [\text{I}^-] = \frac{0 \text{ mol}}{0.0510 \text{ L}} = 0 \text{ M}$$

Now,  $\text{PbI}_2$  is a slightly soluble compound ( $K_{\text{sp}} = 8.7 \times 10^{-9}$ ), and so a part of the  $1.63 \times 10^{-5}$  mol that precipitated will *re-dissolve back* into solution. We need an ICE table to find out how much:

	$\text{PbI}_2 (\text{s})$	$\rightleftharpoons$	$\text{Pb}^{2+}$	+	$2 \text{I}^-$
I	$(1.63 \times 10^{-5} \text{ mol})$		1.665		0
C	$(-s)$		$+s$		$+2s$
E	$(1.63 \times 10^{-5} \text{ mol} - s)$		$1.665 + s$		$2s$

$$K_{\text{sp}} = [\text{Pb}^{2+}][\text{I}^-]^2$$

$$8.7 \times 10^{-9} = (1.665 + s)(2s)^2$$

$$8.7 \times 10^{-9} \approx (1.665)(2s)^2$$

$$s = 3.61 \times 10^{-5} \text{ mol/L}$$

CHECK:  $\frac{3.61 \times 10^{-5}}{1.665} \times 100\% = 0.002\%$

$$[\text{Pb}^{2+}] = 1.665 \text{ M} + s$$

$$= 1.665 + 3.61 \times 10^{-5} \text{ M}$$

$$= 1.66 \text{ M}$$

$$[\text{I}^-] = 2s$$

$$= (2)(3.61 \times 10^{-5}) \text{ M}$$

$$= 7.22 \times 10^{-5} \text{ M}$$

$$[\text{Pb}^{2+}] = \underline{\underline{1.66 \text{ M}}}$$

$$[\text{Na}^+] = \underline{\underline{6.39 \times 10^{-4} \text{ M}}}$$

$$[\text{NO}_3^-] = \underline{\underline{3.33 \text{ M}}}$$

$$[\text{I}^-] = \underline{\underline{7.22 \times 10^{-5} \text{ M}}}$$

c) (3 pts) What mass (in mg) of solid precipitate is obtained?

This part comes from the final line in the ICE table: using the solubility ( $s$ ) and the total volume (51 mL) we find out exactly how many moles of  $\text{PbI}_2$  dissolves back into solution, and subtract from the moles of precipitate found:

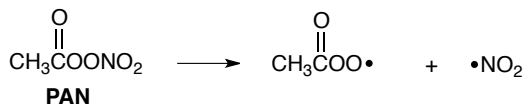
$$\text{mol PbI}_2 \text{ that dissolves} = \frac{3.61 \times 10^{-5} \text{ mol}}{\text{L}} \times 0.0510 \text{ L} = 1.84 \times 10^{-6} \text{ mol}$$

$$\therefore \text{mol PbI}_2 \text{ remaining} = (1.63 \times 10^{-5} - 1.84 \times 10^{-6}) \text{ mol} = 1.45 \times 10^{-5} \text{ mol}$$

$$? \text{ g PbI}_2 = 1.45 \times 10^{-5} \text{ mol} \times \frac{461 \text{ g}}{\text{mol}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 6.7 \text{ mg}$$

Answer: 6.7 mg

3. Peroxyacetyl nitrate (PAN) is an air pollutant produced during photochemical smog events. PAN is unstable and dissociates into peroxyacetyl radicals and nitrogen dioxide.



THIS IS TAKEN FROM MIDTERM 2 2012 AND MIDTERM 2 2014

- a) (3 pts) Using the data in the table below, derive a rate law for the decomposition of PAN at 25.0°C, as well as the value of the rate constant (with appropriate units).

Trial	Initial [PAN] (M)	Initial Rate (M/min)
1	$8.30 \times 10^{-10}$	$1.92 \times 10^{-11}$
2	$1.66 \times 10^{-9}$	$3.84 \times 10^{-11}$
3	$2.49 \times 10^{-9}$	$5.78 \times 10^{-11}$

Or: Trials 1 & 2: [PAN] x 2 → rate x 2  
 Trials 1 & 3: [PAN] x 3 → rate x 3

∴ rate = k[PAN] (it's first order)

$$k = \frac{\text{rate}}{[\text{PAN}]} = \frac{1.92 \times 10^{-11} \text{ M} \cdot \text{min}^{-1}}{8.30 \times 10^{-10} \text{ M}} = 2.31 \times 10^{-2} \text{ min}^{-1}$$

Rate law is: rate = k[PAN]

Rate constant is: k = 0.0231 min<sup>-1</sup>

- b) (2 pts) The decomposition of PAN has a half-life of 35.0 hr at 0.00°C. What is the rate constant for this reaction at this temperature? Use the same units as part (a).

It's first order, so:

$$t_{1/2} = \frac{\ln 2}{k} \quad \therefore k = \frac{\ln 2}{t_{1/2}} = \frac{\ln 2}{35.0 \text{ hr}} \cdot \frac{1 \text{ hr}}{60 \text{ min}} = 3.30 \times 10^{-4} \text{ min}^{-1}$$

Answer: 3.3x10<sup>-4</sup> min<sup>-1</sup>

5. (5 pts) After a vacation of scuba-diving, Dr. Fox has to clean and rinse all her scuba gear before putting it back into storage. She wants to use "Diver's Buddy Scuba Shampoo", a commercially available aqueous solution of trimethylamine ( $\text{N}(\text{CH}_3)_3$ ,  $K_b = 6.31 \times 10^{-6}$ ). Dr. Fox measures the pH of the solution and finds it to be 10.55. What is the concentration of trimethylamine in the shampoo, in mol/L?

THIS IS A STANDARD "HERE'S THE CONCENTRATION OF A WEAK ACID OR WEAK BASE, FIND THE pH" QUESTION, BUT IN REVERSE

$$\text{pOH} = 14 - \text{pH} = 3.45$$

$$[\text{OH}^-] = 10^{-3.45} = 3.55 \times 10^{-4} \text{ M}$$

Let B represent the base,  $\text{N}(\text{CH}_3)_3$ .

	B	+ H <sub>2</sub> O	$\rightleftharpoons$	OH <sup>-</sup>	+ HB <sup>+</sup>
I	[B] <sub>o</sub>	-		0	0
C	-x	-		+x	+x
E	[B] <sub>o</sub> - x	-		x	x

$$x = [\text{OH}^-] = 3.55 \times 10^{-4} \text{ M}$$

$$K_b = \frac{[\text{OH}^-][\text{HB}^+]}{[\text{B}]}$$

$$6.31 \times 10^{-6} = \frac{x^2}{[\text{B}]_o - x} \approx \frac{x^2}{[\text{B}]_o}$$

$$\therefore 6.31 \times 10^{-6} = \frac{(3.55 \times 10^{-4})^2}{[\text{B}]_o}$$

$$[\text{B}]_o = 0.0200 \text{ M}$$

$$\text{Check: } \frac{3.55 \times 10^{-4}}{0.0200} \times 100\% = 1.8\% \longrightarrow \text{PASSES}$$

Answer: 0.020 M

## 1. Short Answer Questions.

a) (0.5 pt) 1.0 mol of an ideal gas is placed in a 1.0 L flask at 22°C. Which of the following would result in the greatest increase in the pressure of the gas?

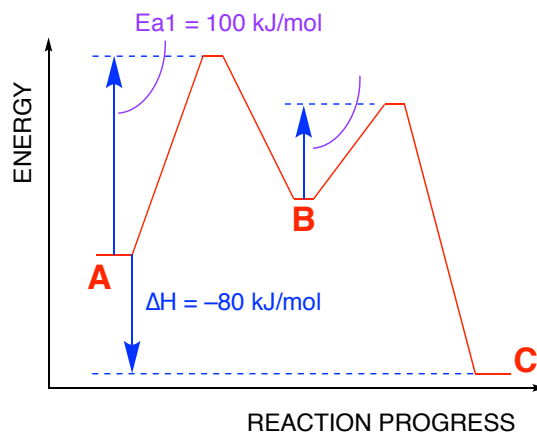
- reducing the volume of the container to 0.50 L
- increasing the amount of gas to 1.5 mol
- increasing the temperature to 300°C

b) (1.5 pts) For an endothermic contraction of a gas:

- |                              |                 |          |         |
|------------------------------|-----------------|----------|---------|
| • The value of W is          | <b>POSITIVE</b> | NEGATIVE | UNKNOWN |
| • The value of q is          | <b>POSITIVE</b> | NEGATIVE | UNKNOWN |
| • The value of $\Delta U$ is | <b>POSITIVE</b> | NEGATIVE | UNKNOWN |

c) (3 pts) On the axes provided at right, draw a line (or curve) representing the reaction profile for a reaction  $A \rightarrow C$  with the following characteristics:

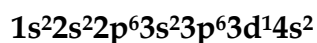
- a two-step mechanism,  $A \rightarrow B$ , then  $B \rightarrow C$
- $E_a$  of step 2 = 50 kJ/mol
- step 1 is two times slower than step 2
- $\Delta H = -80$  kJ/mol



On your profile, label the following: A, B, C,  $E_{a1}$  (for step 1),  $E_{a2}$  (for step 2), and  $\Delta H$ .

d) (0.5 pt) Below is a hypothetical configuration for the ground state of a scandium atom.

This configuration is incorrect because:



- it contains one or more orbitals that do not exist
- it contains too few electrons
- it contains too many electrons
- it contains electrons in incorrect orbitals
- it contains orbitals listed in incorrect order

e) (1 pt) The number of atoms in 10.0 g of  $\text{CaCO}_3$  (100.0 g/mol) is:

$$1.81 \times 10^{23}$$

$$6.02 \times 10^{22}$$

$$3.01 \times 10^{23}$$

$$1.21 \times 10^{23}$$

- f) (1 pt) The cheese on a pizza stays hot for a long time, while the crust cools down more quickly, making it possible for you to hold the pizza slice, yet still burn your mouth on the cheese. Which substance has the smaller specific heat capacity?

**CRUST**

**CHEESE**

- g) (2.5 pt) Phosphorous acid has  $pK_{a1} = 1.30$  and  $pK_{a2} = 6.70$ . An aqueous solution of this acid is titrated with NaOH (aq). At the *first* equivalence point, the pH of the solution will be

**ACIDIC**

**BASIC**

**NEUTRAL**

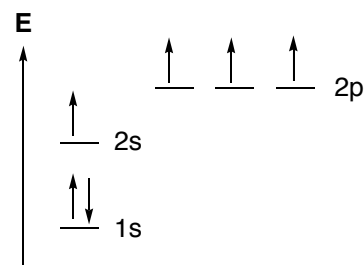
Write the equation for the expected hydrolysis:

The conjugate base,  $H_2PO_3^-$  is amphiprotic. Since  $pK_{a1}$  is lower than  $pK_{b2}$ ,  $H_2PO_3^-$  is a better proton DONOR than proton ACCEPTOR, and so it will act as an acid in water:



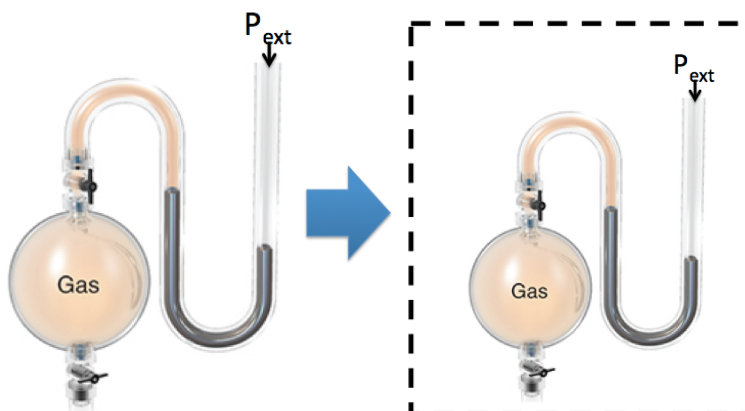
- h) (0.5 pt) A student draws the orbital energy diagram at right for a carbon atom. As shown, this diagram:

- is correct  
 disobeys the Pauli Exclusion Principle  
 disobeys Hund's Rule  
 disobeys the Aufbau Principle



- i) (2 pts) For a first order reaction, the half-life **DOES NOT CHANGE** with increasing reactant concentration. For a second order reaction, the half-life **DECREASES** with increasing reactant concentration.

- j) (1 pt) 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.



k) (1 pt) Solid potassium chromate is slowly added to an aqueous solution that contains 0.200 M each  $\text{Pb}^{2+}$  and  $\text{Ag}^+$  ions. The compound that precipitates first is:  $\text{PbCrO}_4$ .

l) (2 pts) Give the maximum number of electrons that can have the following quantum numbers:

•  $n = 2$  and  $l = 1$                       number of electrons = 6

•  $n = 5$ ,  $l = 5$  and  $m_l = 0$               number of electrons = 0

m) (1 pt) A one litre balloon is filled with neon gas. A hole is made in the balloon and the gas effuses at a rate of 0.0280 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of effusion would be 0.0199 mol/hr.

n) (0.5 pt) It is possible to prepare a buffer by taking a strong base and titrating it with a strong acid to the half equivalence point.      TRUE      FALSE

o) (1 pt) For an ideal gas, a graph of PV versus T will be a linear relationship with a slope that is directly proportional to the gas's:

KINETIC ENERGY

MOLAR MASS

ENTHALPY

MASS

p) (1 pt) Decreasing the temperature of an exothermic reaction will:

- increase the yield and the rate
- increase the yield and decrease the rate
- decrease the yield and increase the rate
- decrease the yield and rate

### BONUS

Complete the following sentence: "Chemists aren't LAZY, we're PRACTICAL!"

2. You wish to prepare a buffer solution with pH = 9.45.

- a) How many grams of  $(\text{NH}_4)_2\text{SO}_4$  would you add to 425 mL of 0.258 M  $\text{NH}_3$  to do this? You may assume that the solution's volume remains constant.  $K_b$  of  $\text{NH}_3 = 1.8 \times 10^{-5}$

$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.5 \times 10^{-10}$$

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) \Rightarrow 9.45 = -\log(5.5 \times 10^{-10}) - \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$\log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) = 9.45 - 9.26 = 0.19 \Rightarrow \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{0.19} = 1.55$$

$$\therefore [\text{NH}_4^+] = 1.55 \times [\text{NH}_3] = 1.55 \times 0.258 \text{ M} = 0.17 \text{ M}$$

$$? \text{ g } (\text{NH}_4)_2\text{SO}_4 = 0.425 \text{ L} \times \frac{0.17 \text{ mol NH}_4^+}{\text{L}} \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4}{2 \text{ mol NH}_4^+} \times \frac{132.1 \text{ g}}{\text{mol}} = 4.8 \text{ g}$$

Answer: 4.8 g

- b) You have access to additional 0.258 M  $\text{NH}_3$  and more solid  $(\text{NH}_4)_2\text{SO}_4$ . Which buffer component, and how much (in g or mL) would you add to 0.100 L of the buffer in part (a) to change its pH to 9.30? You may assume that the solution's volume remains constant.

$$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$9.30 = 9.26 - \log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$\log\left(\frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right) = 9.30 - 9.26 = 0.04 \Rightarrow \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = 10^{0.04} = 1.1$$

So, to lower the pH to 9.30, we'll need to add some acid. But how much?

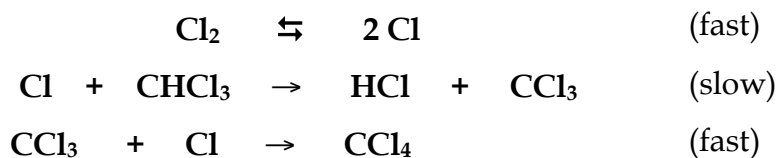
$$[\text{NH}_3] = 0.258 \text{ M} \quad \text{and} \quad [\text{NH}_4^+] = 0.17 \text{ M} + x$$

$$\therefore \frac{[\text{NH}_3]}{[\text{NH}_4^+]} = \frac{0.258}{0.17 + x} = 1.1 \Rightarrow x = 0.062 \text{ M}$$

$$? \text{ g } (\text{NH}_4)_2\text{SO}_4 = 0.100 \text{ L} \times \frac{0.062 \text{ mol NH}_4^+}{\text{L}} \times \frac{1 \text{ mol } (\text{NH}_4)_2\text{SO}_4}{2 \text{ mol NH}_4^+} \times \frac{132.1 \text{ g}}{\text{mol}} = 0.41 \text{ g}$$

Component:  $(\text{NH}_4)_2\text{SO}_4$  Amount: 0.41 g

3. Consider the following three-step mechanism:



a) (2 pts) What is the overall reaction? Identify any reaction intermediates.



**Intermediates =** Cl and CCl<sub>3</sub>

b) (3 pts) The rate law is determined experimentally to be:  $\text{rate} = k[\text{CHCl}_3][\text{Cl}_2]^{1/2}$ . Is the proposed mechanism valid? Why or why not?

**Since the second step is slowest, it must be the RDS. Deriving the expected rate law gives:**

$$\begin{aligned} \text{rate} &= k_2[\text{Cl}][\text{CHCl}_3] \\ k_1[\text{Cl}_2] &= k_{-1}[\text{Cl}]^2 \\ \therefore [\text{Cl}] &= \left(\frac{k_1}{k_{-1}}\right)^{1/2} [\text{Cl}_2]^{1/2} \\ \therefore \text{rate} &= \left(\frac{k_1}{k_{-1}}\right)^{1/2} k_2[\text{Cl}_2]^{1/2}[\text{CHCl}_3] = k_{\text{obs}}[\text{CHCl}_3][\text{Cl}_2]^{1/2} \end{aligned}$$

**Since this matches the experimentally measured rate law, this is a valid mechanism.**

c) (2 pts) When  $[\text{CHCl}_3]_i = 1.05 \times 10^{-4} \text{ M}$  and  $[\text{Cl}_2]_i = 2.64 \text{ M}$ , the initial rate of reaction is  $2.4 \times 10^{-3} \text{ M/s}$ . Find the value of the rate constant, with the appropriate units.

$$\begin{aligned} \text{rate} &= k_{\text{obs}}[\text{CHCl}_3][\text{Cl}_2]^{1/2} \\ \therefore k_{\text{obs}} &= \frac{\text{rate}}{[\text{CHCl}_3][\text{Cl}_2]^{1/2}} = \frac{2.4 \times 10^{-3} \text{ M} \cdot \text{s}^{-1}}{(1.05 \times 10^{-4} \text{ M})(2.64 \text{ M})^{1/2}} = 14.1 \text{ M}^{-1/2} \cdot \text{s}^{-1} \end{aligned}$$

d) (3 pts) What will be  $[\text{CHCl}_3]$  after 12.0 s using the conditions from part c)? HINT: note the relative reactant concentrations!

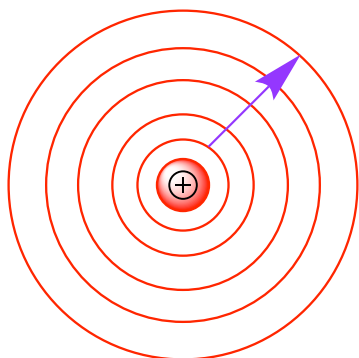
**Since  $[\text{CHCl}_3]_i \ll \ll \ll [\text{Cl}_2]_i$ , we can assume pseudo-first conditions:**

$$\begin{aligned} \text{rate} &= k_{\text{obs}}[\text{CHCl}_3][\text{Cl}_2]^{1/2} \\ k' &= k_{\text{obs}}[\text{Cl}_2]^{1/2} = (14.1 \text{ M}^{-1/2} \cdot \text{s}^{-1})(2.64 \text{ M})^{1/2} = 22.91 \text{ s}^{-1} \\ \therefore \ln[\text{CHCl}_3]_t &= \ln[\text{CHCl}_3]_i - k't = \ln(1.05 \times 10^{-4} \text{ M}) - (22.91 \text{ s}^{-1})(12.0 \text{ s}) = -284.08 \\ \therefore [\text{CHCl}_3]_t &= e^{-284} = 0 \text{ M (the reaction is complete!)} \end{aligned}$$

## 4. Electrons in Atoms.

- a) (4 pts) Draw a diagram of Bohr's model of the hydrogen atom showing the transition of an electron from the  $n = 5$  level to the ground state. What is the change in energy (in kJ/mol) of this transition?

Ground state means  $n = 1$ , therefore the transition is from  $n = 1$  to  $n = 5$ :

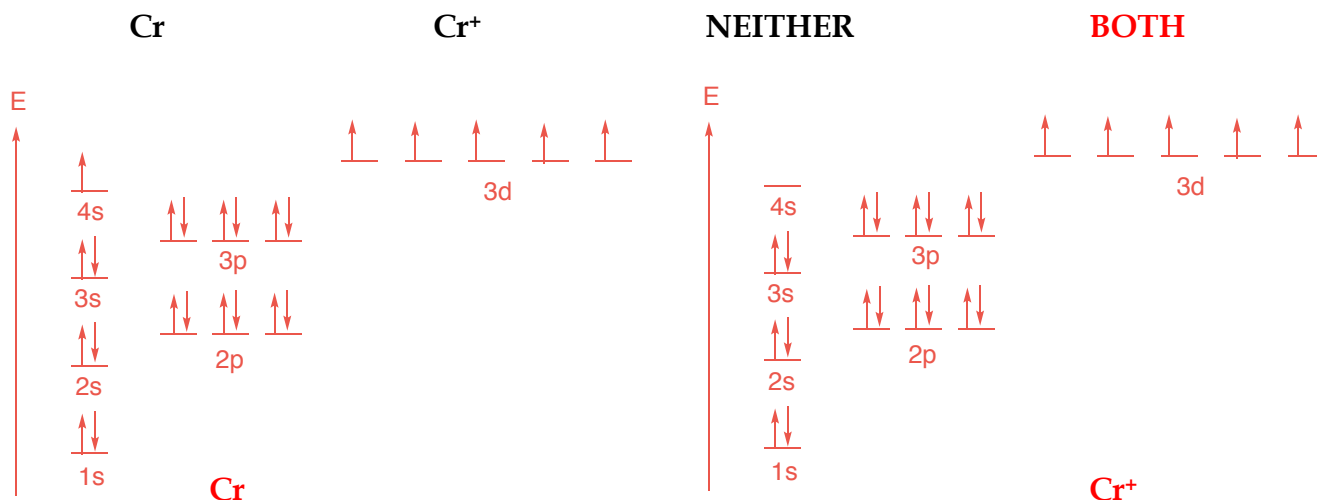


$$\begin{aligned}\Delta E \text{ (in J)} &= -R_H \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) \\ &= (-2.179 \times 10^{-18} \text{ J}) \left( \frac{1}{5^2} - \frac{1}{1^2} \right) \\ &= 2.09 \times 10^{-18} \text{ J} \\ \Delta E \text{ (in kJ/mol)} &= 2.09 \times 10^{-18} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times \frac{6.022 \times 10^{23}}{\text{mol}} \\ &= 1260 \text{ kJ/mol}\end{aligned}$$

- b) (3 pts) Calculate the wavelength (in nm) that corresponds to the energy found in part a).

$$\begin{aligned}\Delta E \text{ (in J)} &= \frac{hc}{\lambda} \\ \lambda \text{ (in nm)} &= \frac{hc}{\Delta E} \\ &= \frac{(6.62608 \times 10^{-34} \text{ J}\cdot\text{s})(2.99792458 \times 10^8 \text{ m}\cdot\text{s}^{-1})}{2.09 \times 10^{-18} \text{ J}} \times \frac{10^9 \text{ nm}}{1 \text{ m}} \\ &= 95.0 \text{ nm}\end{aligned}$$

- c) (4 pts) Between Cr and Cr<sup>+</sup>, which species is expected to be paramagnetic? Circle your answer below. To obtain full marks, draw the orbital energy diagram for each species.



5. The age of rocks is sometimes calculated from the measured excess of lead-206 atoms over the normal abundance. Lead-206 has a natural abundance of 23.6%.

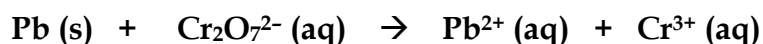
a) (1 pt) Write the atomic symbol for lead-206 in the form  ${}^A_Z X$ :  ${}^{206}_{82} \text{Pb}$

b) (5 pts) What volume block of lead (in  $\text{cm}^3$ ) will contain  $8.34 \times 10^{21}$  atoms of lead-206? The density of lead is  $11.35 \text{ g/cm}^3$ .

$$\begin{aligned} ? \text{ cm}^3 \text{ Pb} &= 8.34 \times 10^{21} \text{ atoms } {}^{206}\text{Pb} \times \frac{100 \text{ atoms Pb}}{23.6 \text{ atoms } {}^{206}\text{Pb}} \times \frac{\text{mol Pb}}{6.022 \times 10^{23} \text{ atoms Pb}} \times \frac{207.2 \text{ g Pb}}{\text{mol Pb}} \times \frac{\text{cm}^3}{11.35 \text{ g}} \\ &= 1.07 \text{ cm}^3 \end{aligned}$$

Answer: \_\_\_\_\_

c) (4 pts) The lead atoms can be extracted from pulverized rock dust via the aqueous redox reaction shown below. Balance the equation, under acidic conditions (including phases).



6. Methanol, CH<sub>3</sub>OH, is synthesized directly on the industrial scale by the reaction of carbon monoxide with hydrogen gas.

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



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

	$\Delta H^\circ_f$ (kJ/mol)
CO(g)	-110.5
CO <sub>2</sub> (g)	-393.5
H <sub>2</sub> (g)	0.0
H <sub>2</sub> O(g)	-241.8
CH <sub>3</sub> OH(g)	-200.7
CH <sub>4</sub> (g)	-74.87

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

Answer: \_\_\_\_\_ **- 90.2 kJ/mol** \_\_\_\_\_

c) (4 pts) The value of the equilibrium constant for the above reaction at 298 K is  $2.27 \times 10^4$ . Calculate the value of the equilibrium constant at 500 K.

$$K_1 = 2.27 \times 10^4 \quad @ T_1 = 298 \text{ K}$$

$$K_2 = ? \quad @ T_2 = 500 \text{ K}$$

Using the van't Hoff Equation:

$$\ln\left(\frac{K_2}{K_1}\right) = -\frac{\Delta H^\circ}{R} \left(\frac{1}{T_2} - \frac{1}{T_1}\right)$$

$$\ln\left(\frac{K_2}{2.27 \times 10^4}\right) = -\frac{-90\,200 \text{ J/mol}}{8.3145 \text{ J/mol} \cdot \text{K}} \left(\frac{1}{500 \text{ K}} - \frac{1}{298 \text{ K}}\right)$$

$$\therefore K_2 = 9.31 \times 10^{-3}$$

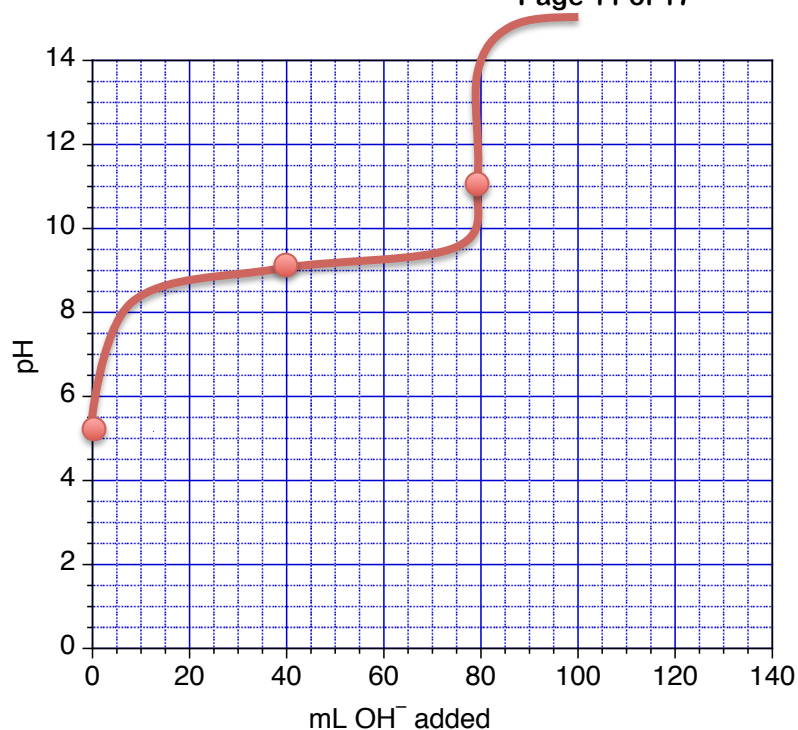
Answer: \_\_\_\_\_ **9.31x10<sup>-3</sup>** \_\_\_\_\_

d) (2 pts) 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. You are performing a titration of 80.0 mL of 0.0900 M HCN with 0.0900 M NaOH. Determine the pH of the solution:

- (3 pts) initially
- (2 pts) at the half-equivalence point
- (4 pts) at the equivalence point
- (1 pt) Use these values to sketch a titration curve on the graph provided.



a) initial pH:

	HA	+ H <sub>2</sub> O	⇌	H <sub>3</sub> O <sup>+</sup>	+ A <sup>-</sup>
I	0.090	-		0	0
C	-x	-		+x	+x
E	0.090 - x	-		x	x

$$\text{pH} = -\log(0.00000747) = 5.13 \text{ @ } 0 \text{ mL}$$

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$6.2 \times 10^{-10} = \frac{x^2}{0.090 - x} \approx \frac{x^2}{0.090}$$

$$\therefore x \approx 7.47 \times 10^{-6} \text{ M} = [\text{H}_3\text{O}^+]$$

$$\text{Check: } \frac{7.47 \times 10^{-6}}{0.090} \times 100\% = 0.008\% \longrightarrow \text{PASSES}$$

b) At the  $\frac{1}{2}$  equivalence point:  $\text{pH} = \text{p}K_a = -\log(6.2 \times 10^{-10}) = 9.21$  (after 40 mL added)

c) At the equivalence point:

mol HA = mol OH<sup>-</sup> added = 0.0072 mol (this corresponds to adding 80.0 mL of base)  
 new [A<sup>-</sup>] = 0.0072 mol / (0.080 L + 0.080 L) = 0.0450 M

Hypochlorite ion (OCl<sup>-</sup>) is the conjugate base of a weak acid, so it hydrolyzes:

	A <sup>-</sup>	+ H <sub>2</sub> O	⇌	HA	+ OH <sup>-</sup>
I	0.045	-		0	0
C	-x	-		+x	+x
E	0.045 - x	-		x	x

$$\text{pOH} = -\log(8.5 \times 10^{-4}) = 3.07$$

$$\text{pH} = 14 - 3.07 = 10.93$$

$$K_b = \frac{K_w}{K_a} = \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]}$$

$$\frac{1.0 \times 10^{-14}}{6.2 \times 10^{-10}} = 1.6 \times 10^{-5} = \frac{x^2}{0.045 - x} \approx \frac{x^2}{0.045}$$

$$\therefore x \approx 8.5 \times 10^{-4} \text{ M} = [\text{OH}^-]$$

$$\text{Check: } \frac{8.5 \times 10^{-4}}{0.045} \times 100\% = 1.8\% \longrightarrow \text{PASSES}$$

8. A student mixes 40.0 mL of 0.0122 M  $\text{Pb}(\text{NO}_3)_2$  (aq) with 40.0 mL of 1.76 M  $\text{KCl}$  (aq).

- a) (1 pt) Identify the expected precipitate:  $\text{PbCl}_2$
- b) (8 pts) What are the values of  $[\text{Pb}^{2+}]$ ,  $[\text{K}^+]$ ,  $[\text{NO}_3^-]$  and  $[\text{Cl}^-]$  after the solution has reached equilibrium at 25°C? You may assume volumes are additive.

**FOR A FULL SOLUTION, SEE MIDTERM 2 KEY**

? mol  $\text{Pb}^{2+} = 4.88 \times 10^{-4}$  mol  
 ? mol  $\text{NO}_3^- = 9.76 \times 10^{-4}$  mol  
 ? mol  $\text{K}^+ = ?$  mol  $\text{Cl}^- = 0.0704$  mol  
 $V_{\text{TOT}} = 0.0800$  L

	$\text{Pb}^{2+}$	+	$2 \text{Cl}^-$	$\rightarrow$	$\text{PbCl}_2$ (s)
B	$4.88 \times 10^{-4}$				0
A			0.0704		
M	$-4.88 \times 10^{-4}$		$-2 \times \{4.88 \times 10^{-4}\}$		$+4.88 \times 10^{-4}$
A	0		0.0694		$4.88 \times 10^{-4}$

**New  $[\text{Cl}^-] = 0.0694 \text{ mol} / 0.0800 \text{ L} = 0.8675 \text{ M}$**

	$\text{PbCl}_2$ (s)	$\rightleftharpoons$	$\text{Pb}^{2+}$	+	$2 \text{Cl}^-$
I	(m)		0		0.8675
C	(-s)		+s		+2s
E	(m-s)		s		$0.8675 + 2s$

$K_{\text{sp}} = [\text{Pb}^{2+}][\text{Cl}^-]^2$   
 $1.9 \times 10^{-5} = (s)(0.8675 + 2s)^2$   
 $1.9 \times 10^{-5} \approx (s)(0.8675)^2$   
 $s = 2.52 \times 10^{-5} \text{ mol/L}$  (PASSES)

$[\text{Pb}^{2+}] = s = 2.5 \times 10^{-5} \text{ M}$   
 $[\text{K}^+] = 0.0704 \text{ mol} / 0.0800 \text{ L} = 0.88 \text{ M}$   
 $[\text{NO}_3^-] = 9.76 \times 10^{-4} \text{ mol} / 0.0800 \text{ L} = 0.122 \text{ M}$   
 $[\text{Cl}^-] = (0.8675 + 2s) = 0.87 \text{ M}$

- c) (3 pts) What mass (in mg) of solid precipitate is obtained?

mol  $\text{PbCl}_2$  that dissolves =  $\frac{2.52 \times 10^{-5} \text{ mol}}{\text{L}} \times 0.0800 \text{ L} = 2.016 \times 10^{-6} \text{ mol}$   
 $\therefore$  mol  $\text{PbCl}_2$  remaining =  $(4.88 \times 10^{-4} - 2.016 \times 10^{-6}) \text{ mol} = 4.86 \times 10^{-4} \text{ mol}$   
 ? mg  $\text{PbCl}_2 = 4.86 \times 10^{-4} \text{ mol} \times \frac{278 \text{ g}}{\text{mol}} \times \frac{1000 \text{ mg}}{1 \text{ g}} = 135 \text{ mg}$

**Answer:** \_\_\_\_\_

9. In the Haber synthesis of ammonia,  $\text{N}_2$  and  $\text{H}_2$  react at high temperature to produce  $\text{NH}_3$ .

a) (6 pts) In a typical reaction, 45.0 kg of  $\text{H}_2$  and 160.0 kg of  $\text{N}_2$  react to produce 152 kg of  $\text{NH}_3$ . Find the percent yield of the reaction, and the mass of *unreacted*  $\text{N}_2$  (in kg).

	$\text{N}_2 + 3 \text{H}_2 \rightarrow 2 \text{NH}_3$		
mass (kg)	160.0	45.0	152
molar mass (g/mol)	28.00	2.016	17.02
mol	5714	22321	8931

$$? \text{ theo. mol NH}_3 \text{ from N}_2 = 5714 \text{ mol N}_2 \times \frac{2 \text{ mol NH}_3}{1 \text{ mol N}_2} = 11428 \text{ mol}$$

$$? \% \text{ yield NH}_3 = \frac{8931 \text{ mol}}{11428 \text{ mol}} \times 100\% = 78\%$$

$$? \text{ mol N}_2 \text{ reacted} = 8931 \text{ mol NH}_3 \times \frac{1 \text{ mol N}_2}{2 \text{ mol NH}_3} = 4465 \text{ mol}$$

$$? \text{ kg N}_2 \text{ leftover} = (5714 \text{ mol} - 4465 \text{ mol}) \times \frac{28.00 \text{ g N}_2}{1 \text{ mol N}_2} \times \frac{1 \text{ kg}}{1000 \text{ g}} = 125 \text{ kg}$$

Percent Yield = 78%      Mass of  $\text{N}_2$  = 125 kg

b) (4 pts) One of the major industrial products of ammonia is urea,  $\text{NH}_2\text{CONH}_2$ . Calculate the molarity of a 1.70 mol/kg aqueous solution of urea. The density of the solution is 1.2 g/mL.

1.70 m means there are 1.70 moles of urea in 1 kg (or 1000 g) of water.

	$\text{NH}_2\text{CONH}_2$	$\text{H}_2\text{O}$
mol	1.70	55.5
molar mass (g/mol)	60.0	18.02
mass (g)	102	1000

The total mass of solution = 102 g + 1000 g = 1102 g

$$? \text{ L solution} = 1102 \text{ g solution} \times \frac{\text{mL solution}}{1.2 \text{ g solution}} \times \frac{1 \text{ L}}{1000 \text{ mL}} = 0.918 \text{ L}$$

$$\therefore C_{\text{urea}} = \frac{1.70 \text{ mol}}{0.918 \text{ L}} = 1.85 \text{ mol/L}$$