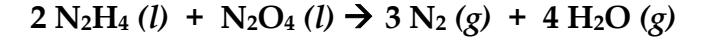
CHM1311 A **Name :** _____

TWO STAGE DGD QUIZ (FRIDAY)

October 6 2017

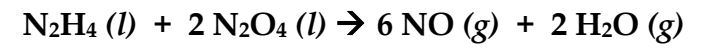
STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. **The equation below represents a fuel mixture reaction used in the early days of rocketry:**



$$2\ N_2H_4\ (l)\ +\ N_2O_4\ (l) \rightarrow 3\ N_2\ (g)\ +\ 4\ H_2O\ (g)$$

However, a second, competing side reaction occasionally occurs, where the fuel produces nitrogen monoxide instead:



$$N_2H_4\ (l)\ +\ 2\ N_2O_4\ (l) \rightarrow 6\ NO\ (g)\ +\ 2\ H_2O\ (g)$$

   a) **(3 pts) If exactly 100.0 g of each reactant is used, what is the theoretical yield of N_2 (in g)?**
   b) **(4 pts) In one trial using the above reactant amounts, a chemical engineer notes that 12.0 g of nitrogen monoxide formed. What is the highest percent yield of nitrogen gas that can be expected from the main reaction?**

Mass of N_2 (theoretical) = _____ **Percent Yield =** _____

2. In an environmental test for lead in soil, the lead is undergoes redox chemistry in acidic solution, according to the following reaction:

$$5\ Pb\ (s)\ +\ 2\ MnO_4^-\ (aq)\ +\ 16\ H^+\ (aq)\ \rightarrow\ 5\ Pb^{2+}\ (aq)\ +\ 2\ Mn^{2+}\ (aq)\ +\ 8\ H_2O\ (aq)$$

a) (1 pt) Indicate above the oxidizing agent and the reducing agent.

b) (1 pt) The name of the MnO_4^- ion is: _____

c) (3 pts) A 25.0 g sample of soil was found to react with 10.06 mL of a 0.120 M $KMnO_4$ solution. What was the percent composition by mass of lead in the soil sample?

Mass percent = _____

3. (3 pts) Complete the following table:

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
Rb	85				+1
		22	20	26	

Question	1 (/8)	2 (/5)	3 (/2)	TOTAL (/15)
Score				

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A
Midterm #1
Fall 2017

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.

Cellular phones, unauthorized electronic devices or course notes (unless an open-book exam) are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

By signing below, you acknowledge that you have ensured that you are complying with the above statement.

Signature: _____

1. Short Answer Questions

a) (0.5 pts) Which compound has the highest oxidation state of nitrogen?

NO^+ N_2 NO_3^- NO_2 N_2O NH_3

b) (1.5 pts) The standard heat of formation of solid potassium perchlorate is -432.8 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? ΔU ΔH q W

d) (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?

a. **reducing the volume of the container to 0.50 L**
b. **increasing the amount of gas to 1.5 mol**
c. **increasing the temperature to 300°C**

e) (1 pt) An aqueous solution of sulphuric acid has a concentration of 0.650 mol/kg. The mole fraction of H_2SO_4 in this mixture is : _____.

f) (1 pt) Two objects of identical mass and size, A and B, absorb the same amount of heat when placed in an oven. However, the temperature of A increases more than B. This is because _____.

(1 pt) BONUS:

Which answer(s) is/are true when comparing 1.0 mol of H_2 (g) and 1.0 mol of He (g), both at STP? The two gases have equal:

- **volumes** **TRUE** **FALSE**
- **root-mean-squared speeds** **TRUE** **FALSE**
- **masses** **TRUE** **FALSE**
- **densities** **TRUE** **FALSE**

2. Complete combustion of a 1.119 g sample of an unknown gaseous compound (consisting of C, H, and S) yields 2.020 g of CO_2, 0.689 g of H_2O, and some SO_2.

a) (6 pts) Find the number of moles of each element in the sample.

C = _____ H = _____ S = _____

b) (1 pt) What is the empirical formula of the compound?

c) (3 pts) A 0.234 g sample of the gas in a 40.0 mL container has a pressure of 0.9986 bar at 300.0 K. What is the molar mass of the unknown compound?

Answer: _____

d) (1 pt) What is the molecular formula of the compound?

3. Elemental tin can be isolated from basic solutions using the following half reactions:

$$Sn(OH)_3^- (aq) \rightarrow Sn (s)$$

$$Fe(OH)_2 (s) \rightarrow Fe(OH)_3 (s)$$

a) (4 pts) Determine the balanced chemical equation for the overall redox reaction.

b) (1 pt) Identify the oxidizing agent and the reducing agent in your reaction above.

c) (4 pts) 1.093 g of $Fe(OH)_2$ is added to 120.0 mL of a 0.0894 M aqueous basic solution of $Sn(OH)_3^-$ and 0.633 g of solid tin is obtained. What was the yield of the redox reaction?

Answer: _____

4. Carbon monoxide can be further oxidized to carbon dioxide according to the reaction:

$$CO(g) + \tfrac{1}{2} O_2(g) \rightarrow CO_2(g) \qquad \Delta H^o = -283.02 \text{ kJ/mol}$$

a) (3 pts) What is the change in internal energy for the oxidation of one mole of CO at 298 K under constant pressure conditions?

Answer: _____

b) (2 pts) Draw a representative energy diagram for this reaction. Fully label your diagram, including: ΔU, U_1, U_2, q, and W.

5. In a constant-pressure calorimeter, 65.0 mL of 0.900 M H_2SO_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 ΔH for this reaction (per mole of H_2O produced)? You may assume that the total volume is the sum of the individual volumes.

Answer: _____

Question	Points Possible	Points Earned	TA Initial
1	5		
2	11		
3	9		
4	5		
5	5		
TOTAL	35		

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A
Midterm #2
Fall 2017

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.

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Signature: _____

1. Short Answer Questions

a. (0.5 pt) Bond breaking is always an exothermic process. TRUE FALSE

b. (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.

c. (2 pts) From the list below, circle the basic salts and underline the neutral salts.

KCl $FeCl_3$ NH_4Br

$Ca(CN)_2$ LiF $CuNO_3$

d. (1 pt) For the reaction $2\ A \leftrightarrows B + 3\ C$ the value of K is 44.5 at 25°C. The value of K for the reaction $2\ B + 6\ C \leftrightarrows 4\ A$ would be _____.

e. (1 pt) For the following three hydrofluoric acid solutions, underline the one with the highest percent ionization and circle the one with the lowest pH.

0.100 M HF 0.500 M HF 0.050 M HF 0.010 M HF

BONUS:

HA^- is an amphiprotic species. When added to water, the two equilibria below are possible. Circle the expected dominant equilibrium and determine if its equilibrium constant is less than or greater than 1. For H_2A, $pK_{a1} = 6.62$ and $pK_{a2} = 12.96$.

To receive all bonus points, show your reasoning.

$$HA^-\ (aq) + H_2O\ (l) \leftrightarrows A^{2-}\ (aq) + H_3O^+\ (aq)$$

$$HA^-\ (aq) + H_2O\ (l) \leftrightarrows H_2A\ (aq) + OH^-\ (aq)$$

K > 1 K < 1

2. Consider the following reaction: $A(g) + 2\,B(g) \leftrightarrows C(g)$

To a 2.40 L flask, A and B are added at initial pressures of 0.400 bar each. The mixture was allowed to equilibrate at 1000 K and the flask was found to contain 0.00444 mol of C.

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

b) (2 pts) What is the percent yield of C?

c) (1 pt) If the equilibrated gas mixture was then transferred to a container of smaller volume, what would be the resulting effect on the equilibrium?

SHIFT TOWARDS REACTANTS SHIFT TOWARDS PRODUCTS NO EFFECT

3. Your lab TA asks you to prepare a buffer solution with a pH of 5.10. The following reagents are all available to you: 500 mL of 0.250 M hydrofluoric acid, 500 mL of 0.250 M acetic acid, solid sodium fluoride and solid sodium acetate.

a) (1 pt) Which 2 ingredients will you use to prepare the desired buffer?

b) (2 pts) What is the base/acid ratio in the desired buffer?

Answer: _____

c) (3 pts) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?

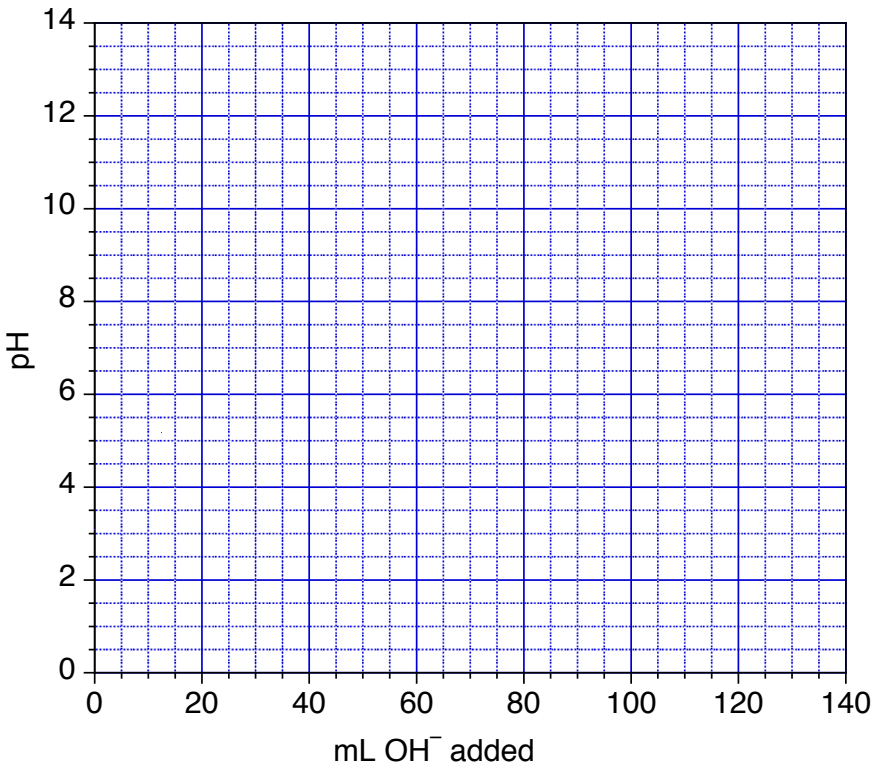
Answer: _____

d) (3 pts) If 5.00 mL of 1.00 M HCl is added to the buffer solution, what will be the new pH?

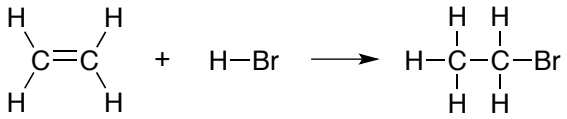
Answer: _____

4. You are performing a titration of 80.0 mL of 0.120 M HN_3 with 0.120 M NaOH. Determine the pH of the solution:

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



5. (4 pts) With the table of bond energies, estimate the energy change of the following 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–H	412	C–Br	276

Answer: _____

Question	Points Possible	Points Earned	TA Initial
1	5		
2	7		
3	9		
4	10		
5	4		
TOTAL	35		

LAST name: _____

FIRST name: _____

Student Number: _____

Seat Number: _____

CHM 1311 A
Final Exam
December 2017

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.

Cellular phones, unauthorized electronic devices or course notes are not allowed during this exam. Phones and devices must be turned off and put away in your bag. Do not keep them in your possession, such as in your pockets. If caught with such a device or document, the following may occur: academic fraud allegations will be filed which may result in you obtaining a 0 (zero) for the exam.

By signing below, you acknowledge that you have ensured that you are complying with the above statement.

Signature: _____

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

1. Short Answer Questions.

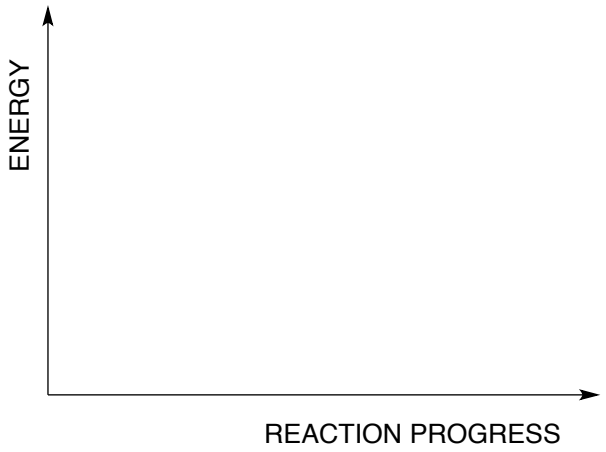
a) (0.5 pt) 1.0 mol of an ideal gas is placed in a 1.0 L flask at 22°C. Which of the following would result in the greatest increase in the pressure of the gas?

- ☐ **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 expansion of a gas:

- **The value of W is** **POSITIVE** **NEGATIVE** **UNKNOWN**
- **The value of q is** **POSITIVE** **NEGATIVE** **UNKNOWN**
- **The value of ΔU is** **POSITIVE** **NEGATIVE** **UNKNOWN**

c) (2 pts) On the axes provided at right, draw a line (or curve) representing the reaction profile for an endothermic reaction following a two-step mechanism, where the second step is the rate-determining step.



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

This configuration is incorrect because: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

- ☐ **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) Which of the following isotopes has the greatest number of neutrons?

$^{35}_{17}Cl$ $^{40}_{19}K$ $^{37}_{17}Cl$ $^{40}_{20}Ca$

f) (2 pts) Classify each of the following reaction conditions as *possible* or *impossible*.

$0 < \Delta H < E_a$ $\Delta H < 0 < E_a$ $0 < E_a < \Delta H$ $0 = \Delta H < E_a$

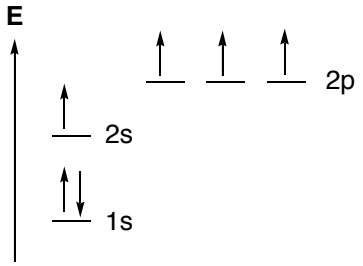
g) (1.5 pts) Ammonia has a $pK_b = 4.74$. An aqueous solution of this base is titrated with HCl (aq). At the equivalence point, the pH of the solution will be:

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) (1 pt) 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) (3 pts) Determine the overall balanced redox reaction (acidic conditions) from the following half reactions:

$$Al \rightarrow Al_2O_3$$

$$Cu^+ \rightarrow Cu$$

OVERALL: _____

k) (1 pt) A solution contains 0.050 M Pb^{2+}. The minimum iodide concentration needed to observe the formation of a solid precipitate is: _____

l) (2 pts) A potassium atom is ionized to form a potassium ion, K^+. Give a possible full set of quantum numbers for the removed electron:

n = _____ l = _____ m_l = _____ m_s= _____

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) The ideal gas law works best at low temperatures and high pressures.

TRUE FALSE

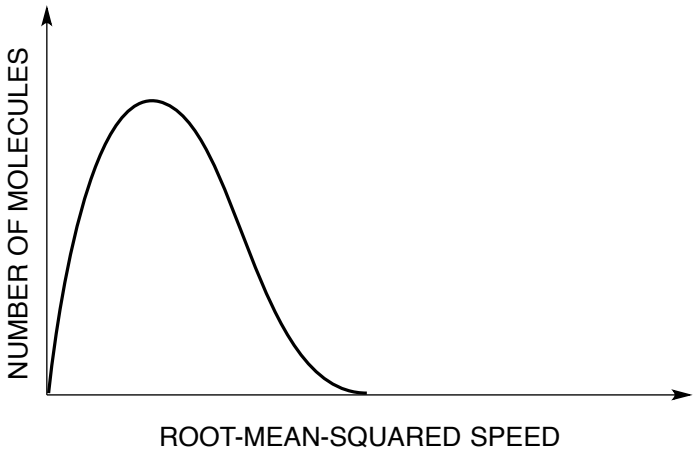
o) (2 pts) Name two ways to accelerate a chemical reaction:

i. _____

ii. _____

BONUS

Below is the distribution of molecular speeds for nitrogen gas at room temperature. On the graph, sketch the expected outcome if the temperature is raised. Explain your new curve, in one or two sentences.



2. Barium sulfate is used in medical imaging of the gastrointestinal tract because it is opaque to X rays. A barium sulfate solution is ingested by the patient, whose stomach and intestines can then be visualized via X-ray imaging.

a) (5 pts) If a patient ingests 200 mL of a saturated barium sulfate solution, how many toxic Ba^{2+} ions has the patient consumed?

b) (3 pts) There are some data that suggest that zinc lozenges can significantly shorten the duration of a cold. If the solubility of zinc acetate, $Zn(CH_3COO)_2$, is 43.0 g/L, what is the K_{sp} of this compound?

c) (2 pts) How might one use pH to improve the solubility of zinc acetate? Explain, using Le Chatelier's Principle.

3. Consider the following three-step mechanism:

$$2\,NO \leftrightarrows N_2O_2 \quad \text{(fast)}$$

$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \quad \text{(slow)}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O \quad \text{(fast)}$$

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

b) (3 pts) The rate law is determined experimentally to be: rate = $k[NO]^2[H_2]$. Is the proposed mechanism valid? Why or why not?

c) (2 pts) When $[NO]_i$ = 5.88 M and $[H_2]_i = 1.00\times10^{-4}$ M, the initial rate of reaction is 3.0×10^{-4} M/s. Find the value of the rate constant, with the appropriate units.

d) (3 pts) What will be $[H_2]$ after 3.00 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 ground state to the n = 4 level. 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 Cu and Cu^+, which species is expected to be paramagnetic? Circle your answer below. To obtain full marks, draw the orbital energy diagram for each species.

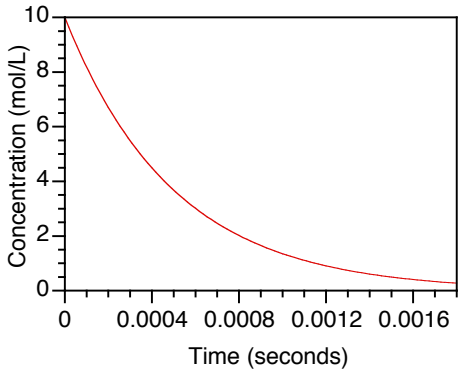
Cu **Cu^+** **NEITHER** **BOTH**

5. A hydrocarbon fuel containing only H and C is being considered as a possible energy source.

a) (4 pts) What is the molar mass of the gas if a 1.000 L flask containing 2.33 g of the gas at 25.0°C has a pressure of 600 mmHg?

b) (3 pts) Elemental analysis of the fuel indicates that each molecule contains exactly 5 carbon atoms. What is the molecular formula of the fuel?

c) (3 pts) The combustion of this hydrocarbon, in the presence of excess oxygen, follows *first order* kinetics, as shown in the graph below. What is the rate constant for the combustion?



6. 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) (4 pts) 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.

b) (2 pts) Calculate the internal energy change for the dissolution, in kJ/mol.

c) (4 pts) Determine the enthalpy change for the following reaction, using the provided data. $X(s) \rightarrow 2Y(s)$ $\Delta H^\circ = ?$

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

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 7.20 L tanks of NITROX by mixing 25.0 g of O_2 with 42.0 g of N_2 at a temperature of 25.0°C.

a) (4 pts) What is the mole fraction of each gas in the mixture?

χ of N_2 = _____ χ of O_2 = _____

b) (4 pts) What is the partial pressure of each gas, in bar?

P of N_2 = _____ P of O_2 = _____

c) (2 pts) What will be the total pressure left in the tank after Dr. Fox breathes 85% of it by volume during a dive?

8. Your lab TA asks you to prepare a buffer solution with a pH of 4.25. The following reagents are all available to you: 500 mL of 0.110 M hydrofluoric acid, 500 mL of 0.110 M acetic acid, solid sodium fluoride and solid sodium acetate.

a) (1 pt) Which 2 ingredients will you use to prepare the desired buffer?

b) (2 pts) What is the base/acid ratio in the desired buffer?

c) (3 pts) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?

d) (3 pts) If 20.00 mL of 1.00 M HCl is added to the buffer solution, what will be the new pH?

9. Shoppers Drug Mart sells has a wide range of products to help ease cold symptoms.

a) (5 pts) One product sold is a homeopathic cough syrup (100 mL bottle for about $8) that contains antimony at a concentration of "14 CH". This corresponds to a ratio of 1.00 g of antimony to 10^{28} g of syrup. How many bottles of this cough syrup must you drink in order to consume one atom of antimony? The cough syrup has a density of 3.12 g/mL.

b) (3 pts) Shoppers also sells prescription-grade Robitussin cough syrup, which contains codeine ($C_{18}H_{21}NO_3$) at a concentration of 0.200% mass by volume. Convert this value to molarity.

c) (2 pts) Rubbing alcohol, used to disinfect cuts and scrapes, is a mixture of isopropanol (C_3H_8O, d = 0.786 g/mL) and water. What is the molality of a solution made from mixing 700 g of isopropanol with 1000 g of water?

CHM1311 A **Name :** _____

TWO STAGE DGD QUIZ (FRIDAY)

October 6 2017

STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. **The equation below represents a fuel mixture reaction used in the early days of rocketry:**

$$2\ N_2H_4\ (l)\ +\ N_2O_4\ (l) \rightarrow 3\ N_2\ (g)\ +\ 4\ H_2O\ (g)$$

However, a second, competing side reaction occasionally occurs, where the fuel produces nitrogen monoxide instead:

$$N_2H_4\ (l)\ +\ 2\ N_2O_4\ (l) \rightarrow 6\ NO\ (g)\ +\ 2\ H_2O\ (g)$$

   a) **(3 pts) If exactly 100.0 g of each reactant is used, what is the theoretical yield of N_2 (in g)?**
   b) **(4 pts) In one trial using the above reactant amounts, a chemical engineer notes that 12.0 g of nitrogen monoxide formed. What is the highest percent yield of nitrogen gas that can be expected from the main reaction?**

THIS QUESTION WAS COVERED IN DGD #2

a) This part is a simple limiting reagent-type problem:

$$?\ \text{mol}\ N_2\ (\text{from}\ N_2H_4) = 100.0\ \text{g}\ N_2H_4 \times \frac{\text{mol}\ N_2H_4}{32.05\ \text{g}\ N_2H_4} \times \frac{3\ \text{mol}\ N_2}{2\ \text{mol}\ N_2H_4} = 4.688\ \text{mol}$$

$$?\ \text{mol}\ N_2\ (\text{from}\ N_2O_4) = 100.0\ \text{g}\ N_2O_4 \times \frac{\text{mol}\ N_2O_4}{92.02\ \text{g}\ N_2O_4} \times \frac{3\ \text{mol}\ N_2}{1\ \text{mol}\ N_2O_4} = 3.261\ \text{mol}$$

Therefore, N_2O_4 is the limiting reagent.

$$?\ \text{g}\ N_2 = 3.261\ \text{mol}\ N_2 \times \frac{28.0\ \text{g}\ N_2}{\text{mol}\ N_2} = 91.3\ \text{g}$$

b) First, we need to find how much N_2O_4 was wasted in the side reaction, then subtract this amount from the initial amount of N_2O_4 available to find the amount of N_2O_4 actually used to make N_2 gas. Then, we can find the mass of N_2 actually formed and thus the yield:

$$?\ \text{mol}\ N_2O_4\ \text{lost in side reaction} = 12.0\ \text{g NO} \times \frac{\text{mol NO}}{30.01\ \text{g NO}} \times \frac{2\ \text{mol}\ N_2O_4}{6\ \text{mol NO}} = 0.1333\ \text{mol}$$

$$?\ \text{mol}\ N_2O_4\ \text{actually reacted} = \left(100.0\ \text{g}\ N_2O_4 \times \frac{\text{mol}\ N_2O_4}{92.02\ \text{g}\ N_2O_4}\right) - 0.1333\ \text{mol} = 0.954\ \text{mol}$$

$$?\ \text{mol}\ N_2\ \text{actually formed} = 0.954\ \text{mol}\ N_2O_4 \times \frac{3\ \text{mol}\ N_2}{1\ \text{mol}\ N_2O_4} \times \frac{28.0\ \text{g}\ N_2}{\text{mol}\ N_2} = 80.1\ \text{g}$$

$$\%\ \text{yield} = \frac{80.1\text{g}}{91.3\text{g}} \times 100\% = 87.7\%$$

Mass of N_2 (theoretical) = _____ **Percent Yield =** _____

2. **In an environmental test for lead in soil, the lead is undergoes redox chemistry in acidic solution, according to the following reaction:**

$$5\ Pb\ (s)\ +\ 2\ MnO_4^-\ (aq)\ +\ 16\ H^+\ (aq)\ \rightarrow\ 5\ Pb^{2+}\ (aq)\ +\ 2\ Mn^{2+}\ (aq)\ +\ 8\ H_2O\ (aq)$$

Pb = red. agent; MnO_4^- = oxidizing agent

a) **(1 pt) Indicate above the oxidizing agent and the reducing agent.**

b) **(1 pt) The name of the MnO_4^- ion is: ____permanganate_____**

c) **(3 pts) A 25.0 g sample of soil was found to react with 10.06 mL of a 0.120 M $KMnO_4$ solution. What was the percent composition by mass of lead in the soil sample?**

THIS QUESTION IS AN IN-CLASS ECHO360 QUESTION

$$?\ g\ Pb = 0.01006\ L\ soln \times \frac{0.120\ mol\ KMnO_4}{L\ soln} \times \frac{1\ mol\ MnO_4^-}{1\ mol\ KMnO_4} \times \frac{5\ mol\ Pb}{2\ mol\ MnO_4^-} \times \frac{207.2\ g\ Pb}{mol\ Pb} = 0.6253\ g$$

$$\%\ mass = \frac{0.6253\ g}{25.0\ g} \times 100\% = 2.50\%$$

3. **(3 pts) Complete the following table:**

THIS QUESTION IS BASED ON SILBERBERG SUGGESTED PROBLEM 2.41

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
Rb	85	37	36	48	+1
Ti	48	22	20	26	+2

Question	1 (/7)	2 (/5)	3 (/3)	TOTAL (/15)
Score				

1. Short Answer Questions

a) (0.5 pts) Which compound has the highest oxidation state of nitrogen?

NO^+ N_2 NO_3^- NO_2 N_2O NH_3

b) (1.5 pts) The standard heat of formation of solid potassium perchlorate is -432.8 kJ. Write the chemical equation for the reaction to which this value applies.

$K(s) + \frac{1}{2} Cl_2(g) + 2 O_2(g) \rightarrow KClO_4(s)$

c) (0.5 pt) Which of the following is/are a state function? ΔU ΔH q W

d) (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?

a. reducing the volume of the container to 0.50 L
b. increasing the amount of gas to 1.5 mol
c. increasing the temperature to 300°C

e) (1 pt) An aqueous solution of sulphuric acid has a concentration of 0.650 mol/kg. The mole fraction of H_2SO_4 in this mixture is : _____0.0116_____.

f) (1 pt) Two objects of identical mass and size, A and B, absorb the same amount of heat when placed in an oven. However, the temperature of A increases more than B. This is because ___A has a lower specific heat capacity than B ($q = mc\Delta T$)_____.

(1 pt) BONUS:

Which answer(s) is/are true when comparing 1.0 mol of H_2 (g) and 1.0 mol of He (g), both at STP? The two gases have equal:

- **volumes** TRUE FALSE
- **root-mean-squared speeds** TRUE FALSE
- **masses** TRUE FALSE
- **densities** TRUE FALSE

2. Complete combustion of a 1.119 g sample of an unknown gaseous compound (consisting of C, H, and S) yields 2.020 g of CO_2, 0.689 g of H_2O, and some SO_2.

THIS QUESTION IS FROM MIDTERM 1 2016

a) (6 pts) Find the number of moles of each element in the sample.

$$? \text{ mol C} = 2.020 \text{ g } CO_2 \times \frac{\text{mol } CO_2}{44.01 \text{ g } CO_2} \times \frac{1 \text{ mol C}}{1 \text{ mol } CO_2} = 0.0460 \text{ mol C}$$

$$? \text{ mol H} = 0.689 \text{ g } H_2O \times \frac{\text{mol } H_2O}{18.02 \text{ g } H_2O} \times \frac{2 \text{ mol H}}{1 \text{ mol } H_2O} = 0.0765 \text{ mol H}$$

$$? \text{ g C} = 0.0460 \text{ mol C} \times \frac{12.011 \text{ g C}}{1 \text{ mol C}} = 0.552 \text{ g C}$$

$$? \text{ g H} = 0.0765 \text{ mol H} \times \frac{1.008 \text{ g H}}{1 \text{ mol H}} = 0.0771 \text{ g H}$$

$$\therefore ? \text{ g S} = 1.119 \text{ g sample} - 0.552 \text{ g C} - 0.0771 \text{ g H} = 0.0490 \text{ g S}$$

$$? \text{ mol S} = 0.0490 \text{ g S} \times \frac{1 \text{ mol S}}{32.066 \text{ g S}} = 0.0153 \text{ mol O}$$

C = 0.0460 mol **H =** 0.0765 mol **S =** 0.0153 mol

b) (1 pt) What is the empirical formula of the compound?

$$C_{\frac{0.0460}{0.0153}} H_{\frac{0.0765}{0.0153}} O_{\frac{0.0153}{0.0153}} = C_3H_5S$$

c) (3 pts) A 0.234 g sample of the gas in a 40.0 mL container has a pressure of 0.9986 bar at 300.0 K. What is the molar mass of the unknown compound?

$$n = \frac{PV}{RT} = \frac{0.9986 \text{ bar} \times 0.0400 \text{ L}}{0.083145 \text{ L} \cdot \text{atm} \cdot \text{mol}^{-1} \cdot \text{K}^{-1} \times 300.0 \text{ K}} = 0.00160 \text{ mol}$$

$$\therefore MM = \frac{0.231 \text{ g}}{0.00160 \text{ mol}} = 146 \text{ g/mol}$$

Answer: 146 g/mol

d) (1 pt) What is the molecular formula of the compound?

$$n = \frac{\text{MF mass}}{\text{EF mass}} = \frac{146}{73} = 2 \qquad \therefore C_3H_5S \times 2 = C_6H_{10}S_2$$

3. Elemental tin can be isolated from basic solutions using the following half reactions:

$$Sn(OH)_3^- (aq) \rightarrow Sn (s)$$

$$Fe(OH)_2 (s) \rightarrow Fe(OH)_3 (s)$$

THIS IS SILBERBERG PROBLEM 19.16c AND WAS ON THE 2015 MIDTERM #1

a) (4 pts) Determine the balanced chemical equation for the overall redox reaction.

$$Sn(OH)_3^- (aq) \rightarrow Sn (s)$$

$$3OH^- (aq) + 3H^+ (aq) + Sn(OH)_3^- (aq) \rightarrow Sn (s) + 3 H_2O (l) + 3 OH^- (aq)$$

$$2e^- (aq) + Sn(OH)_3^- (aq) \rightarrow Sn (s) + 3 OH^- (aq)$$

$$Fe(OH)_2 (s) \rightarrow Fe(OH)_3 (s)$$

$$Fe(OH)_2 (s) + OH^- (aq) \rightarrow Fe(OH)_3 (s) + e^-$$

$$2 Fe(OH)_2 (s) + 2 OH^- (aq) \rightarrow 2 Fe(OH)_3 (s) + 2 e^-$$

$$2 Fe(OH)_2 (s) + Sn(OH)_3^- (aq) \rightarrow Sn(s) + 2 Fe(OH)_3 (s) + OH^- (aq)$$

reducing agent oxidizing agent

b) (1 pt) Identify the oxidizing agent and the reducing agent in your reaction above.

c) (4 pts) 1.093 g of $Fe(OH)_2$ is added to 120.0 mL of a 0.0894 M aqueous basic solution of $Sn(OH)_3^-$ and 0.633 g of solid tin is obtained. What was the yield of the redox reaction?

THIS IS VERY SIMILAR TO AN ECHO360 QUESTION DONE IN CLASS

$$\text{? g Sn from } Fe(OH)_2 = 1.093 \text{ g } Fe(OH)_2 \times \frac{\text{mol } Fe(OH)_2}{89.86 \text{ g } Fe(OH)_2} \times \frac{1 \text{ mol Sn}}{2 \text{ mol } Fe(OH)_2} \times \frac{118.7 \text{ g Sn}}{\text{mol Sn}}$$

$$= 0.722 \text{ g}$$

$$\text{? g Sn from } Sn(OH)_3^- = 0.1200 \text{ L solution} \times \frac{0.0894 \text{ mol } Sn(OH)_3^-}{\text{L solution}} \times \frac{1 \text{ mol Sn}}{1 \text{ mol } Sn(OH)_3^-} \times \frac{118.7 \text{ g Sn}}{\text{mol Sn}}$$

$$= 1.27 \text{ g}$$

Therefore, $Fe(OH)_2$ is the limiting reagent.

$$\% \text{ yield} = \frac{0.633 \text{ g}}{0.722 \text{ g}} \times 100\% = 87.7\%$$

Answer: _____

4. Carbon monoxide can be further oxidized to carbon dioxide according to the reaction:

$$CO(g) + \tfrac{1}{2}\,O_2(g) \rightarrow CO_2(g) \qquad \Delta H^\circ = -283.02\ kJ/mol$$

a) (3 pts) What is the change in internal energy for the oxidation of one mole of CO at 298 K under constant pressure conditions?

THIS IS SIMILAR TO A QUESTION SOLVED IN CLASS, AND I COVERED A SIMILAR PROBLEM IN THE OCT 9 DGD, AND IT APPEARED ON THE 2010 MIDTERM #1

$$q = 1\ mol\ CO \times \frac{-283.02\ kJ}{mol} = -283.02\ kJ$$

$$W = -P\Delta V$$

$$= -\Delta nRT$$

$$= -(1 - 1.5\ mol)(8.3145\ J/mol\ K)(298\ K)$$

$$= +1239\ J$$

$$= 1.24\ kJ$$

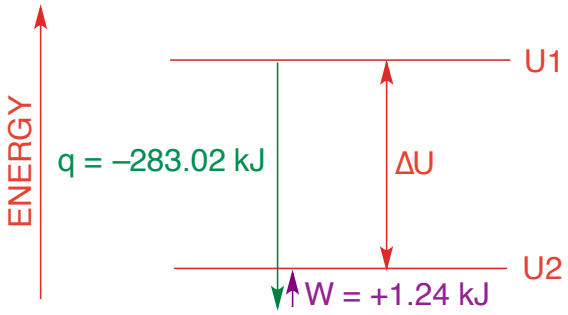
$$\Delta U = q + W$$

$$= -283.02\ kJ + 1.24\ kJ$$

$$= -281.78\ kJ$$

Answer: ____–281.78 kJ_____

b) (2 pts) Draw a representative energy diagram for this reaction. Fully label your diagram, including: ΔU, U_1, U_2, q, and W.



Note that this reaction is an exothermic contraction,
but because q is so much larger than W, overall, ΔU is NEGATIVE.

5. In a constant-pressure calorimeter, 65.0 mL of 0.900 M H_2SO_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 TAKEN FROM SAPLING ASSIGNMENT #5, AND IS ALSO VERY SIMILAR TO A QUESTION SOLVED IN THE OCT 9 DGD

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

$$H_2SO_4\,(aq) + 2\,NaOH \rightarrow Na_2SO_4\,(aq) + 2\,H_2O\,(l)$$

b) (4 pts) If the solution has the same density and specific heat as water, what is ΔH for this reaction (per mole of H_2O produced)? You may assume that the total volume is the sum of the individual volumes.

$$?\ \text{mol } H_2O \text{ from } H_2SO_4 = 0.065\ \text{L soln} \times \frac{0.900\ \text{mol } H_2SO_4}{\text{L soln}} \times \frac{2\ \text{mol } H_2O}{1\ \text{mol } H_2SO_4} = 0.117\ \text{mol}$$

$$?\ \text{mol } H_2O \text{ from NaOH} = 0.065\ \text{L soln} \times \frac{0.250\ \text{mol NaOH}}{\text{L soln}} \times \frac{2\ \text{mol } H_2O}{2\ \text{mol NaOH}} = 0.01625\ \text{mol}$$

Therefore, the NaOH is the limiting reagent.

$$q_{reaction} = -q_{surr}$$

$$= -m_{total} \times c \times \Delta T$$

$$= -(130\ \text{g} \times \frac{1\ \text{mL}}{1\ \text{g}})(4.184\ \text{J/g}^{\circ}\text{C})(25.30^{\circ}\text{C} - 23.60^{\circ}\text{C})$$

$$= -924.7\ \text{J}$$

$$\Delta H = \frac{q}{n} = \frac{-924.7\ \text{J}}{0.01625\ \text{mol}} = -56.9\ \text{kJ/mol}$$

Answer: _____**-56.9 kJ/mol**_____

1. Short Answer Questions

a. **(0.5 pt) Bond breaking is always an exothermic process. TRUE FALSE**

b. **(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.**

c. **(2 pts) From the list below, circle the basic salts and underline the neutral salts.**

KCl	$FeCl_3$	NH_4Br
$Ca(CN)_2$	LiF	$CuNO_3$

d. **(1 pt) For the reaction $2\ A \leftrightarrows B + 3\ C$ the value of K is 44.5 at 25°C. The value of K for the reaction $2\ B + 6\ C \leftrightarrows 4\ A$ would be** $K' = 1/K^2 = 5.05 \times 10^{-4}$.

e. **(1 pt) For the following three hydrofluoric acid solutions, underline the one with the highest percent ionization and circle the one with the lowest pH.**

0.100 M HF 0.500 M HF 0.050 M HF 0.010 M HF

BONUS:

HA^- is an amphiprotic species. When added to water, the two equilibria below are possible. Circle the expected dominant equilibrium and determine if its equilibrium constant is less than or greater than 1. For H_2A, $pK_{a1} = 6.62$ and $pK_{a2} = 12.96$.

To receive all bonus points, show your reasoning.

EQM #1: $HA^-(aq) + H_2O(l) \leftrightarrows A^{2-}(aq) + H_3O^+(aq)$

EQM #2: $HA^-(aq) + H_2O(l) \leftrightarrows H_2A(aq) + OH^-(aq)$

$K > 1$ $K < 1$

(BELOW IS A FULL-LENGTH EXPLANATION, THE KEY POINTS ARE IN BLUE)

Since H_2A is a diprotic acid, we can write two equilibria for its ionization:

$H_2A(aq) + H_2O(l) \leftrightarrows HA^-(aq) + H_3O^+(aq)$ $pK_{a1} = 6.62$ $K_{a1} = 2.4\times10^{-7}$

$HA^-(aq) + H_2O(l) \leftrightarrows A^{2-}(aq) + H_3O^+(aq)$ $pK_{a2} = 12.96$ $K_{a2} = 1.1\times10^{-13}$

So, EQM #1 above corresponds to the second ionization, with $K = K_{a2} = 1.1\times10^{-13}$

Therefore, A^{2-} is a diprotic base, and we can write two equilibria for its ionization:

$A^{2-}(aq) + H_2O(l) \leftrightarrows HA^-(aq) + OH^-(aq)$ $K_{b1} = K_w/K_{a2} = 9.1\times10^{-2}$

$HA^-(aq) + H_2O(l) \leftrightarrows H_2A(aq) + OH^-(aq)$ $K_{b2} = K_w/K_{a1} = 4.2\times10^{-8}$

So, EQM #2 above corresponds to the second ionization, with $K = K_{b2} = 4.2\times10^{-8}$

Comparing the two: EQM #1 $K_{a2} = 1.1\times10^{-13}$
EQM #2 $K_{b2} = 4.2\times10^{-8}$

Since $K_{b2} > K_{a2}$, EQM #2 will dominate, and its value is less than 1!

2. Consider the following reaction: $A(g) + 2\,B(g) \leftrightarrows C(g)$

To a 2.40 L flask, A and B are added at initial pressures of 0.400 bar each. The mixture was allowed to equilibrate at 1000 K and the flask was found to contain 0.00444 mol of C.

THIS QUESTION IS FROM MIDTERM #1 2016

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

$$P_C \text{ at EQM} = \frac{n_C RT}{V} = \frac{(0.00444\text{ mol})(0.083145\text{ L}\cdot\text{bar/mol}\cdot\text{K})(1000\text{ K})}{2.40\text{ L}}$$

$$= 0.154\text{ bar}$$

	A(g) +	2 B(g) ⇆	C (g)
I	0.400	0.400	0
C	–0.154	–2(0.154)	+0.154
E	0.246	0.092	0.154

$$K_P = \frac{P_C}{(P_A)^2 \times P_B} = \frac{0.154}{(0.246)(0.092)^2} = 74.0$$

b) (2 pts) What is the percent yield of C?

$$\text{? theoretical } P_C \text{ from A} = 0.400\text{ bar A} \times \frac{1\text{ bar C}}{1\text{ bar A}} = 0.400\text{ bar}$$

$$\text{? theoretical } P_C \text{ from B} = 0.400\text{ bar B} \times \frac{1\text{ bar C}}{2\text{ bar B}} = 0.200\text{ bar}$$

Therefore, B is the LIMITING REAGENT.

$$\%\text{ yield} = \frac{0.154\text{ bar}}{0.200\text{ bar}} \times 100\% = 77.0\%$$

c) (1 pt) If the equilibrated gas mixture was then transferred to a container of smaller volume, what would be the resulting effect on the equilibrium?

SHIFT TOWARDS REACTANTS **SHIFT TOWARDS PRODUCTS** **NO EFFECT**

3. Your lab TA asks you to prepare a buffer solution with a pH of 5.10. The following reagents are all available to you: 500 mL of 0.250 M hydrofluoric acid, 500 mL of 0.250 M acetic acid, solid sodium fluoride and solid sodium acetate.

THIS IS A SLIGHTLY MODIFIED VERSION OF AN EXAMPLE IN THE COURSE NOTES

a) (1 pt) Which 2 ingredients will you use to prepare the desired buffer?

CH_3COOH/CH_3COO^- $pK_a = -\log(1.8\times10^{-5}) = 4.74$
HF/F^- $pK_a = -\log(6.6\times10^{-4}) = 3.18$
Therefore, acetic acid/acertate is the appropriate choice.

b) (2 pts) What is the base/acid ratio in the desired buffer?

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$

$$\therefore \frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{pH-pK_a} = 10^{5.10-4.74} = 2.29$$

c) (3 pts) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 2.29$$

$$\therefore [CH_3COO^-] = 2.29 \times [CH_3COOH] = 2.29 \times 0.250\ M = 0.573\ M$$

$$?\ g\ CH_3COONa = 0.500\ L \times \frac{0.573\ mol\ OCl^-}{L} \times \frac{1\ mol\ CH_3COONa}{1\ mol\ CH_3COOH} \times \frac{82.03\ g\ CH_3COONa}{mol\ CH_3COONa}$$

$$= 23.5\ g$$

d) (3 pts) If 5.00 mL of 1.00 M HCl is added to the buffer solution, what will be the new pH?

$$?\ mol\ H_3O^+\ added = 0.00500\ L \times \frac{1.00\ mol\ H_3O^+}{L} = 0.0050\ mol$$

$$?\ mol\ CH_3COOH\ initial = 0.500\ L \times \frac{0.250\ mol\ OCl^-}{L} = 0.1250\ mol$$

$$?\ mol\ CH_3COO^-\ initial = 0.500\ L \times \frac{0.573\ mol\ HOCl}{L} = 0.2865\ mol$$

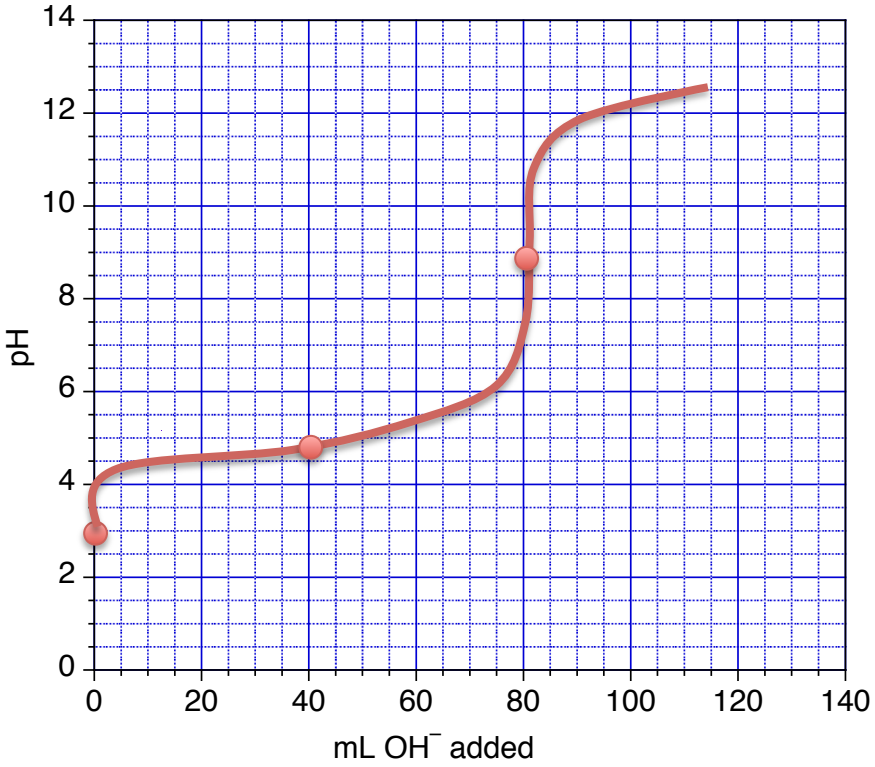
	A^-	+ H_3O^+ ⇆	HA	+ H_2O
B	0.2865		0.1250	-
A		0.0050		-
M	-0.0050	-0.0050	+0.0050	-
A	0.2815	0	0.1300	-

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right) = 4.74 + \log\left(\frac{0.2815}{0.1300}\right) = 5.08$$

4. You are performing a titration of 80.0 mL of 0.120 M HN_3 with 0.120 M NaOH. Determine the pH of the solution:

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

THIS QUESTION IS FROM THE 2015 FINAL EXAM



a) initial pH:

	HA + H_2O ⇆	H_3O^+ +	A^-
I	0.120	0	0
C	$-x$	$+x$	$+x$
E	$0.120 - x$	x	x

$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

$$1.9x10^{-5} = \frac{x^2}{0.120 - x} \approx \frac{x^2}{0.120}$$

$$\therefore x \approx 0.00151\ \text{M} = [H_3O^+]$$

$$\text{Check: } \frac{0.00151}{0.120} \times 100\% = 0.04\% \longrightarrow \text{PASSES}$$

pH = –log(0.00151) = 2.82

b) At the ½ equivalence point: pH = pK_a = –log($1.9x10^{-5}$) = 4.72 (after 40 mL added)

c) At the equivalence point:

mol HA = mol OH^- added = 0.0096 mol (this corresponds to adding 80.0 mL of base)
new $[A^-]$ = 0.0096 mol/(0.080 L + 0.080L) = 0.060 M

Azide (N_3^-) is the conjugate base of a weak acid, so it hydrolyzes:

	A^- + H_2O ⇆	HA +	OH^-
I	0.060	0	0
C	$-x$	$+x$	$+x$
E	$0.060 - x$	x	x

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

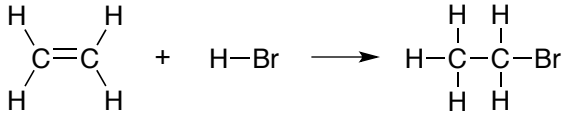
$$\frac{1.0x10^{-14}}{1.9x10^{-5}} = 5.2x10^{-10} = \frac{x^2}{0.060 - x} \approx \frac{x^2}{0.060}$$

$$\therefore x \approx 5.6x10^{-6}\ \text{M} = [OH^-]$$

$$\text{Check: } \frac{5.6x10^{-6}}{0.060} \times 100\% = 0.2\% \longrightarrow \text{PASSES}$$

pOH = –log($5.6x10^{-6}$) = 5.25
pH = 14 – 5.25 = 8.75

5. (4 pts) With the table of bond energies, estimate the energy change of the following 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–H	412	C–Br	276

THIS IS SILBERBERG SUGGESTED PROBLEM 8.50

BROKEN:

1 x C=C	1 x 612 kJ	612 kJ
1 x H-Br	1 x 363 kJ	363 kJ
	TOTAL	+ 975 kJ

FORMED:

1 x C–C	1 x 348 kJ	348 kJ
1 x C–H	1 x 412 kJ	412 kJ
1 x C–Br	1 x 276 kJ	276 kJ
	TOTAL	–1036 kJ

ΔE = +975 kJ + (–1036 kJ) = –61 kJ

Question	Points Possible	Points Earned	TA Initial
1	5		
2	7		
3	9		
4	10		
5	4		
TOTAL	35		

1. Short Answer Questions.

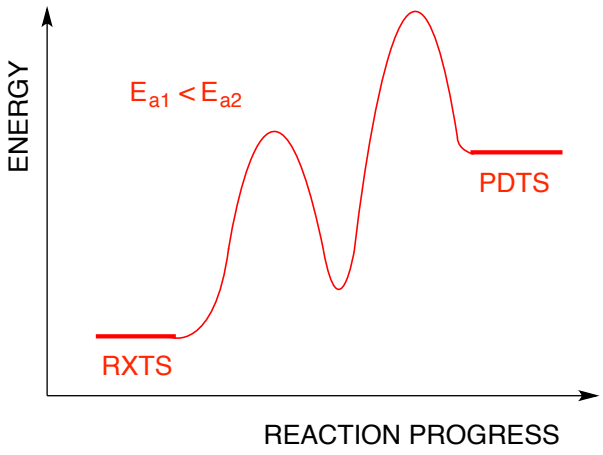
a) (0.5 pt) 1.0 mol of an ideal gas is placed in a 1.0 L flask at 22°C. Which of the following would result in the greatest increase in the pressure of the gas?

- ☐ 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 expansion of a gas:

• The value of W is	POSITIVE	NEGATIVE	UNKNOWN
• The value of q is	POSITIVE	NEGATIVE	UNKNOWN
• The value of ΔU is	POSITIVE	NEGATIVE	UNKNOWN

c) (2 pts) On the axes provided at right, draw a line (or curve) representing the reaction profile for an endothermic reaction following a two-step mechanism, where the second step is the rate-determining step.



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

This configuration is incorrect because: $1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^5$

- ☐ 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) Which of the following isotopes has the greatest number of neutrons?

$^{35}_{17}Cl$ $^{40}_{19}K$ $^{37}_{17}Cl$ $^{40}_{20}Ca$

f) (2 pts) Classify each of the following reaction conditions as *possible* or *impossible*.

$0 < \Delta H < E_a$	$\Delta H < 0 < E_a$	$0 < E_a < \Delta H$	$0 = \Delta H < E_a$
possible	possible	impossible	possible

g) (1.5 pts) Ammonia has a pK_b = 4.74. An aqueous solution of this base is titrated with HCl (aq). At the equivalence point, the pH of the solution will be:

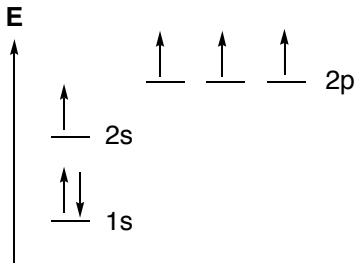
ACIDIC BASIC NEUTRAL

Write the equation for the expected hydrolysis:

$NH_4^+ + H_2O \leftrightarrows NH_3 + H_3O^+$

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) (1 pt) For a first order reaction, the half-life ____IS CONSTANT/DOES NOT CHANGE____ with increasing reactant concentration. For a second order reaction, the half-life ___DECREASES___ with increasing reactant concentration.

j) (3 pts) Determine the overall balanced redox reaction (acidic conditions) from the following half reactions:

$3\ H_2O + 2\ Al \rightarrow Al_2O_3 + 6\ H^+ + 6\ e^-$

$6\ e^- + 6\ Cu^+ \rightarrow 6\ Cu$

OVERALL: _____$3\ H_2O + 2\ Al + 6\ Cu^+ \rightarrow Al_2O_3 + 6\ H^+ + 6\ Cu$_____

k) (1 pt) A solution contains 0.050 M Pb^{2+}. The minimum iodide concentration needed to observe the formation of a solid precipitate is: $[I^-] = \sqrt{(K_{sp}/[Pb^{2+}])} = 4.2 \times 10^{-4}$ M

l) (2 pts) A potassium atom is ionized to form a potassium ion, K^+. Give a possible full set of quantum numbers for the removed electron:

n = ___4____ l = ____0_____ m_l = ____0_____ m_s= ____– ½ or + ½ _____

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 ____0.020 mol/hr_____.

n) (0.5 pt) The ideal gas law works best at low temperatures and high pressures.

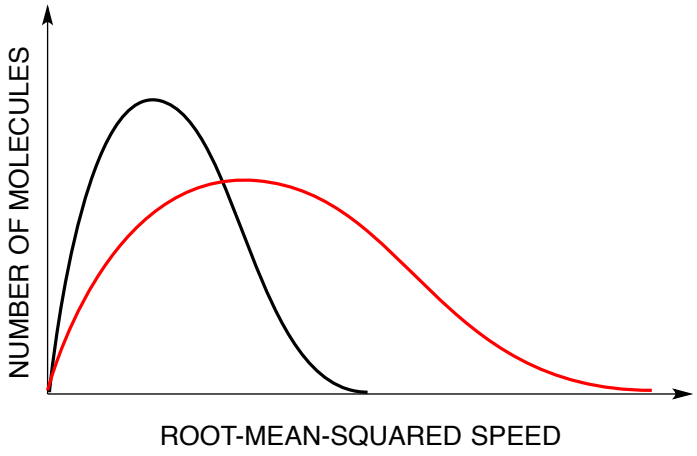
TRUE **FALSE**

o) (2 pts) Name two ways to accelerate a chemical reaction.

- add a catalyst
- increase temperature
- increase reactant concentrations
- increase surface area of reactants

BONUS

Below is the distribution of molecular speeds for nitrogen gas at room temperature. On the graph, sketch the expected outcome if the temperature is raised. Explain your new curve, in one or two sentences.



At a higher temperature, the gas molecules have a greater average kinetic energy ($E_K \propto T$). Thus, proportionally more molecules will be moving with faster speeds, and the curve spreads out to larger values of u_{rms}.

2. Barium sulfate is used in medical imaging of the gastrointestinal tract because it is opaque to X rays. A barium sulfate solution is ingested by the patient, whose stomach and intestines can then be visualized via X-ray imaging.

a) (5 pts) If a patient ingests 200 mL of a saturated barium sulfate solution, how many toxic Ba^{2+} ions has the patient consumed?

K_{sp} of $BaSO_4 = 1.1 \times 10^{-10}$ Let s represent the solubility of barium sulfate:

	$BaSO_4(s)$ ⇆	$Ba^{2+}(aq)$ +	$SO_4^{2-}(aq)$
I	m	0	0
C	–s	+s	+s
E	m – s	s	s

$$K_{sp} = [Ba^{2+}][SO_4^{2-}] = s^2$$

$$s = \sqrt{K_{sp}} = \sqrt{(1.1 \times 10^{-10})} = 1.05 \times 10^{-5}\ M = [Ba^{2+}]$$

$$?\ Ba^{2+}\ ions = 200\ mL \times \frac{1\ L}{1000\ mL} \times \frac{1.05x10^{-5}\ mol\ Ba^{2+}}{L} \times \frac{6.022x10^{23}\ Ba^{2+}\ ions}{mol\ Ba^{2+}\ ions}$$
$$= 1.3x10^{18}\ ions$$

b) (3 pts) There are some data that suggest that zinc lozenges can significantly shorten the duration of a cold. If the solubility of zinc acetate, $Zn(CH_3COO)_2$, is 43.0 g/L, what is the K_{sp} of this compound?

Let s represent the solubility of zinc acetate:

$$s = \frac{?\ mol\ Zn(CH_3COO)_2}{L}$$
$$= \frac{43.0\ g\ Zn(CH_3COO)_2}{1\ L} \times \frac{mol\ Zn(CH_3COO)_2}{183.5\ g\ Zn(CH_3COO)_2}$$
$$= 0.234\ mol/L$$

	$Zn(CH_3COO)_2$ (s) ⇆	$Zn^{2+}(aq)$ +	$2\ CH_3COO^-(aq)$
I	m	0	0
C	–s	+s	+2s
E	m – s	s	2s

$$K_{sp} = [Zn^{2+}][CH_3COO^-]^2 = (s)(2s)^2 = 4s^3 = 4 \times (0.234)^3 = 0.051$$

c) (2 pts) How might one use pH to improve the solubility of zinc acetate? Explain, using Le Chatelier's Principle.

The anion formed in the dissolution, acetate, is the CONJUGATE BASE of a WEAK ACID. Therefore, it will HYDROLYZE when added to water:

$$CH_3COO^- + H_2O \leftrightarrows CH_3COOH + OH^-$$

Thus, this salt will be MORE SOLUBLE in ACIDIC SOLUTIONS (because the acid will consume the produced OH^- and pull the equilibrium forward).

3. Consider the following three-step mechanism:

$$2\,NO \leftrightarrows N_2O_2 \quad \text{(fast)}$$

$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \quad \text{(slow)}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O \quad \text{(fast)}$$

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

Overall reaction = $2\,NO + 2\,H_2 \rightarrow N_2 + 2\,H_2O$

Intermediates = N_2O_2 and N_2O

b) (3 pts) The rate law is determined experimentally to be: rate = k[NO]²[H₂]. 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:

$$\text{rate} = k_2[N_2O_2][H_2]$$

$$k_1[NO]^2 = k_{-1}[N_2O_2]$$

$$\therefore [N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$

$$\therefore \text{rate} = \frac{k_1k_2}{k_{-1}}[NO]^2[H_2] = k_{obs}[NO]^2[H_2]$$

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

c) (2 pts) When $[NO]_i$ = 5.88 M and $[H_2]_i$ = 1.00x10⁻⁴ M, the initial rate of reaction is 3.0x10⁻⁴ M/s. Find the value of the rate constant, with the appropriate units.

$$\text{rate} = k[NO]^2[H_2]$$

$$\therefore k = \frac{\text{rate}}{[NO]^2[H_2]} = \frac{3.0\times10^{-6}\ \text{M}\cdot\text{s}^{-1}}{(6.00\ \text{M})^2(1.00\times10^{-4}\ \text{M})} = 8.33\times10^{-4}\ \text{M}^{-2}\cdot\text{s}^{-1}$$

d) (3 pts) What will be $[H_2]$ after 3.00 s using the conditions from part c)? HINT: note the relative reactant concentrations!

Since $[NO]_i >>> [H_2]_i$, we can assume pseudo-first conditions:

$$\text{rate} = k[NO]^2[H_2]$$

$$k' = k[NO]^2 = (8.33\times10^{-4}\ \text{M}^{-2}\cdot\text{s}^{-1})(6.00\ \text{M})^2 = 0.030\ \text{s}^{-1}$$

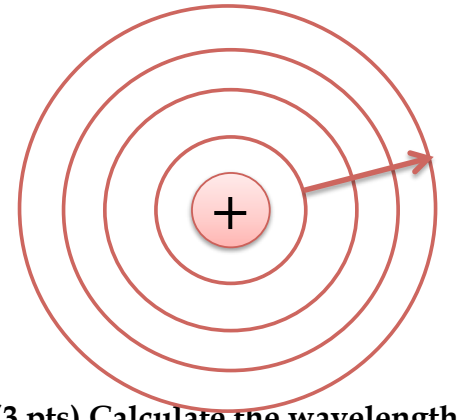
$$\therefore \ln[H_2]_t = \ln[H_2]_i - k't = \ln(1.0\times10^{-4}\ \text{M}) - (0.030\ \text{s}^{-1})(5.00\ \text{s}) = -9.36$$

$$\therefore [H_2]_t = e^{-9.36} = 8.6\times10^{-5}\ \text{M}$$

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 ground state to the n = 4 level. 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 = 4:



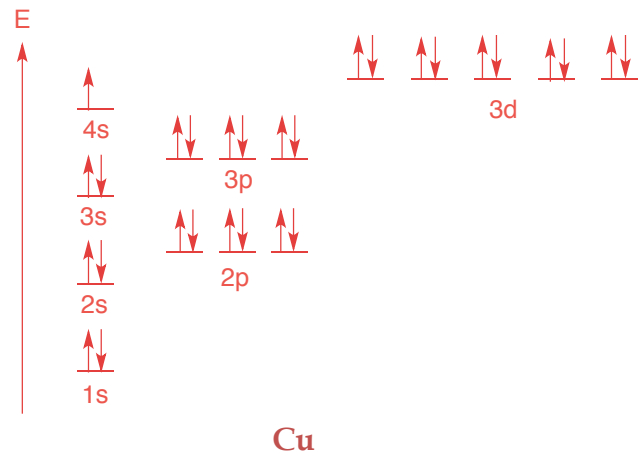
$$\Delta E\ (\text{in J}) = -R_H\left(\frac{1}{n_f^2}-\frac{1}{n_i^2}\right)$$
$$= (-2.179\times10^{-18}\ \text{J})\left(\frac{1}{4^2}-\frac{1}{1^2}\right)$$
$$= 2.04\times10^{-18}\ \text{J}$$
$$\Delta E\ (\text{in kJ/mol}) = 2.04\times10^{-18}\ \text{J}\times\frac{1\ \text{kJ}}{1000\ \text{J}}\times\frac{6.022\times10^{23}}{\text{mol}}$$
$$= 1230\ \text{kJ/mol}$$

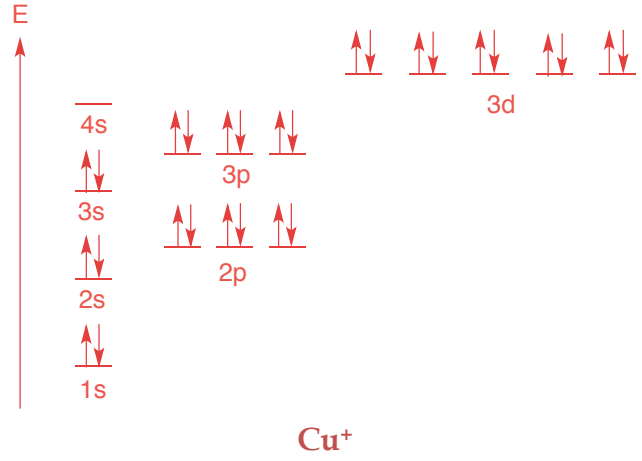
b) (3 pts) Calculate the wavelength (in nm) that corresponds to the energy found in part a).

$$\Delta E\ (\text{in J}) = \frac{hc}{\lambda}$$
$$\lambda\ (\text{in nm}) = \frac{hc}{\Delta E}$$
$$= \frac{(6.62608\times10^{-34}\ \text{J}\cdot\text{s})(2.99792458\times10^{8}\ \text{m}\cdot\text{s}^{-1})}{2.04\times10^{-18}\ \text{J}}\times\frac{10^{9}\ \text{nm}}{1\ \text{m}}$$
$$= 97.4\ \text{nm}$$

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

Cu Cu⁺ NEITHER BOTH





5. A hydrocarbon fuel containing only H and C is being considered as a possible energy source.

a) (4 pts) What is the molar mass of the gas if a 1.000 L flask containing 2.33 g of the gas at 25.0°C has a pressure of 600 mmHg?

Combining:
PV = nRT and n = m/MW
Gives:

$$MW = \frac{mRT}{PV} = \frac{2.33\ g \times 0.08206\ L \cdot atm/mol \cdot K \times 298\ K}{0.790\ atm \times 1.00\ L}$$

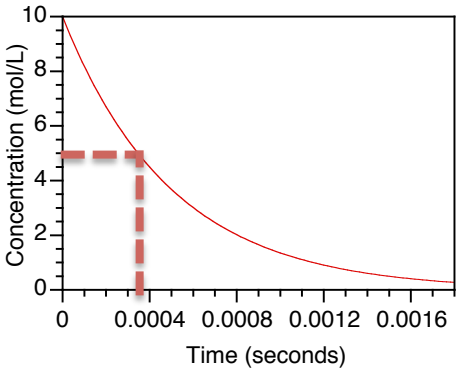
$$= 72.12\ g/mol$$

b) (3 pts) Elemental analysis of the fuel indicates that each molecule contains exactly 5 carbon atoms. What is the molecular formula of the fuel?

5 carbons = 5 x 12.011 g/mol = 60.055 g/mol
The rest is hydrogen:
m of H = 72.12 g/mol – 60.055 g/mol = 12.068 g/mol
Therefore, the number of H's = 12.068/1.0079 = 11.97 ~ 12

C_5H_{12}

c) (3 pts) The combustion of this hydrocarbon, in the presence of excess oxygen, follows *first order* kinetics, as shown in the graph below. What is the rate constant for the combustion?



Since it is first order:

$$t_{1/2} = \frac{\ln 2}{k}$$

$$k = \frac{\ln 2}{0.00035s} = 2.0x10^3\ s^{-1}$$

6. 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) → X(aq)

and the temperature of the solution increases to 28.0°C.

a) (4 pts) 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.

$$q_{soln} = m_{soln} c_{soln} \Delta T_{soln}$$

$$= (2.20\text{g} + 24.0\text{g})(4.184 \frac{\text{J}}{\text{g}^\circ\text{C}})(28.0^\circ\text{C} - 13.0^\circ\text{C})$$

$$= +\ 1644\ \text{J}$$

$$\therefore q_{rxn} = -\ 1644\ \text{J}$$

$$\Delta H^\circ_{rxn} = \frac{?\ \text{kJ}}{\text{mol}} = \frac{-1644\ \text{J}}{2.20\ \text{g}} \times \frac{47.0\ \text{g}}{\text{mol}} \times \frac{1\ \text{kJ}}{1000\ \text{J}} = -35.1\ \text{kJ/mol}$$

b) (2 pts) Calculate the internal energy change for the dissolution, in kJ/mol.

$\Delta U = q + W = \Delta H + W$
But: there are no gases involved. Therefore $W \sim 0$ and thus:
$\Delta U \sim \Delta H = -35.1$ kJ/mol

c) (4 pts) Determine the enthalpy change for the following reaction, using the provided data. X (s) → 2Y (s) ΔH° = ?

Y(s) → Y(aq)	ΔH° = +24.7 kJ
2 Y(aq) → X(aq)	ΔH° = -1.44 kJ

Using the value from part (a):

① (same)	X(s) → X(aq)	ΔH° = –35.1 kJ
③ reversed	X(aq) → 2 Y(aq)	ΔH° = +1.44 kJ
② reversed, x2	2 Y(aq) → 2 Y(s)	ΔH° = -49.4 kJ
SUM	X (s) → 2Y (s)	ΔH° = –83.2 kJ

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 7.20 L tanks of NITROX by mixing 25.0 g of O_2 with 42.0 g of N_2 at a temperature of 25.0°C.

a) (4 pts) What is the mole fraction of each gas in the mixture?

$$?\ \text{mol}\ O_2 = 25.0\ \text{g}\ O_2 \times \frac{\text{mol}\ O_2}{31.998\ \text{g}\ O_2} = 0.781\ \text{mol}\ O_2$$

$$?\ \text{mol}\ N_2 = 42.0\ \text{g}\ N_2 \times \frac{\text{mol}\ N_2}{28.014\ \text{g}\ N_2} = 1.500\ \text{mol}\ N_2$$

$$\text{Total mol}\ n_T = 0.781 + 1.500 = 2.281\ \text{mol}$$

$$\therefore \chi_{N_2} = \frac{1.500\ \text{mol}}{2.281\ \text{mol}} = 0.658$$

$$\therefore \chi_{O_2} = \frac{0.781\ \text{mol}}{2.281\ \text{mol}} = 0.342$$

b) (4 pts) What is the partial pressure of each gas, in bar?

$$P_T = \frac{n_T RT}{V} = \frac{(2.281\ \text{mol})(0.083145\ \text{L}\cdot\text{bar/mol}\cdot\text{K})(298\text{K})}{7.20\ \text{L}}$$
$$= 7.85\ \text{bar}$$

$$P_{N_2} = \chi_{N_2} \times P_T = (0.658)(7.85\ \text{bar})$$
$$= 5.16\ \text{bar}$$

$$P_{O_2} = \chi_{O_2} \times P_T = (0.342)(7.85\ \text{bar})$$
$$= 2.68\ \text{bar}$$

c) (2 pts) What will be the total pressure left in the tank after Dr. Fox breathes 85% of it by volume during a dive?

If 85% has been consumed, there is 15% left.
V_2 is 15% of V_1 → Therefore, P_2 is 15% of P_1
$P_2 = (0.15)(7.85\ \text{bar}) = 1.18\ \text{bar}$

8. Your lab TA asks you to prepare a buffer solution with a pH of 4.25. The following reagents are all available to you: 500 mL of 0.110 M hydrofluoric acid, 500 mL of 0.110 M acetic acid, solid sodium fluoride and solid sodium acetate.

a) (1 pt) Which 2 ingredients will you use to prepare the desired buffer?

CH_3COOH/CH_3COO^- $pK_a = -\log(1.8\times10^{-5}) = 4.74$
HF/F^- $pK_a = -\log(6.6\times10^{-4}) = 3.18$
Therefore, acetic acid/acetate is the appropriate choice.

b) (2 pts) What is the base/acid ratio in the desired buffer?

$$pH = pK_a + \log\left(\frac{[CH_3COO^-]}{[CH_3COOH]}\right)$$
$$\therefore \frac{[CH_3COO^-]}{[CH_3COOH]} = 10^{pH-pK_a} = 10^{4.25-4.74} = 0.3236$$

c) (3 pts) What mass (in g) of solid base must you dissolve in the corresponding acid solution to achieve the desired buffer pH?

$$\frac{[CH_3COO^-]}{[CH_3COOH]} = 0.3236$$
$$\therefore [CH_3COO^-] = 0.3236 \times [CH_3COOH] = 0.3236 \times 0.110\ M = 0.0356\ M$$
$$?\ g\ CH_3COONa = 0.500\ L \times \frac{0.0356\ mol\ CH_3COO^-}{L} \times \frac{1\ mol\ CH_3COONa}{1\ mol\ CH_3COO^-} \times \frac{82.03\ g\ CH_3COONa}{mol\ CH_3COONa}$$
$$= 1.46\ g$$

d) (3 pts) If 20.00 mL of 1.00 M HCl is added to the buffer solution, what will be the new pH?

$$?\ mol\ H_3O^+\ added = 0.02000\ L \times \frac{1.00\ mol}{L} = 0.0200\ mol$$
$$?\ mol\ CH_3COOH\ initial = 0.500\ L \times \frac{0.110\ mol}{L} = 0.0550\ mol$$
$$?\ mol\ CH_3COO^-\ initial = 0.500\ L \times \frac{0.0356\ mol}{L} = 0.0178\ mol$$

	A^-	+ H_3O^+ ⇆	HA	+ H_2O
B	0.0178		0.0550	-
A		0.0200		-
M	-0.0178	-0.0178	+0.0178	-
A	0	0.0022	0.0728	-

This is no longer a buffer (we have exceeded the buffer capacity), and so the pH is determined from the leftover H_3O^+:

$$pH = -\log(0.0022\ mol/0.500\ L) = 2.36$$

9. Shoppers Drug Mart sells has a wide range of products to help ease cold symptoms.

a) (5 pts) One product sold is a homeopathic cough syrup (100 mL bottle for about $8) that contains antimony at a concentration of "14 CH". This corresponds to a ratio of 1.00 g of antimony to 10^{28} g of syrup. How many bottles of this cough syrup must you drink in order to consume one atom of antimony? The cough syrup has a density of 3.12 g/mL.

$$\frac{?\text{ atoms Sb}}{\text{L syrup}} = \frac{1.00\text{ g Sb}}{10^{28}\text{ g syrup}} \times \frac{\text{mol Sb}}{121.76\text{ g Sb}} \times \frac{6.022\text{x}10^{23}\text{ atoms Sb}}{\text{mol Sb}} \times \frac{3.12\text{ g syrup}}{\text{mL syrup}} \times \frac{1000\text{ mL syrup}}{\text{L syrup}}$$

$$= 0.00154\text{ atoms Sb/L}$$

$$?\text{ bottles} = 1\text{ atom Sb} \times \frac{1\text{ L}}{0.00154\text{ atoms Sb}} \times \frac{1000\text{ mL}}{1\text{ L}} \times \frac{1\text{ bottle}}{100\text{ mL}}$$

$$= 6480\text{ bottles}$$

b) (3 pts) Shoppers also sells prescription-grade Robitussin cough syrup, which contains codeine ($C_{18}H_{21}NO_3$) at a concentration of 0.200% mass by volume. Convert this value to molarity.

$$\frac{?\text{ mol } C_{18}H_{21}NO_3}{\text{L solution}} = \frac{0.200\text{ g } C_{18}H_{21}NO_3}{100\text{ mL solution}} \times \frac{\text{mol } C_{18}H_{21}NO_3}{299.358\text{ g } C_{18}H_{21}NO_3} \times \frac{1000\text{ mL}}{1\text{ L}}$$

$$= 0.00668\text{ mol/L}$$

c) (2 pts) Rubbing alcohol, used to disinfect cuts and scrapes, is a mixture of isopropanol (C_3H_8O, d = 0.786 g/mL) and water. What is the molality of a solution made from mixing 700 g of isopropanol with 1000 g of water?

$$\frac{?\text{ mol } C_3H_8O}{\text{kg water}} = \frac{700\text{ g } C_3H_8O}{1000\text{ g water}} \times \frac{\text{mol } C_3H_8O}{60.094\text{ g } C_3H_8O} \times \frac{1000\text{ g water}}{1\text{ kg water}}$$

$$= 11.6\text{ mol/kg}$$