CHM1311 A **Name :** _____

TWO STAGE DGD QUIZ (MONDAY)

October 3 2016

STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. **(6 pts) Elemental phosphorus, P_4, reacts vigorously with molecular oxygen to give P_4O_{10}. Calculate the mass of P_4O_{10} that can be prepared from 3.75 g of P_4 and 6.55 g of O_2. Identify the excess reactant and calculate how many grams of it remains at the end of the reaction.**

Mass of P_4O_{10} = _____ **Excess reactant and mass =** _____

2. (4 pts) What is the mole fraction of ethyl alcohol (C_2H_6O, density = 0.79 g/ml) in water for a solution made from equal volumes of each liquid?

Mole fraction = _____

3. (5 pts) Balance the following half-reaction in basic solution. No phases required.

$$Se + Cr(OH)_3 \rightarrow SeO_3^{2-} + Cr$$

Question	1 (/6)	2 (/4)	3 (/5)	TOTAL (/15)
Score				

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A
Midterm #1
Fall 2016

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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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	5		
2	11		
3	10		
4	5		
5	4		
TOTAL	35		

1. Short Answer Questions

a) (1.5 pts) In the following redox reaction, label the oxidation states of each element and circle the oxidizing agent:

$$N_2H_4\,(aq) + 2\,Zn^{2+}\,(aq) + 4OH^-\,(aq) \rightarrow N_2\,(g) + 2\,Zn\,(s) + 4\,H_2O\,(l)$$

b) (0.5 pt) In the reaction: N_2O_4 (g) ⇆ 2 NO_2 (g) (ΔH = 57.2 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. 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

c) (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

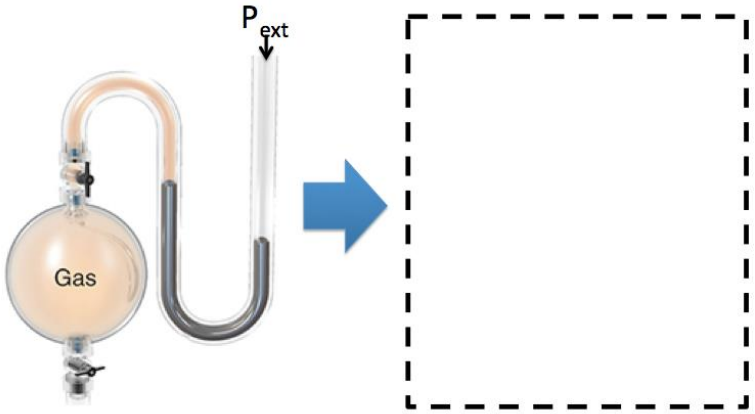
d) (1 pt) Toothpaste contains 0.24% m/v sodium fluoride. This concentration expressed in mol/L is: _____

e) (1.5 pts) Complete the following table:

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
As	70				+3

(1 pt) BONUS:

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



2. Complete combustion of a 1.505 g sample of an unknown gaseous compound (consisting of C, H, and S) yields 3.149 g of CO_2, 0.645 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 0.178 g sample of the gas in a 25.0 mL container has a pressure of 1.055 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. 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) (5 pts) What is the total pressure in the flask at equilibrium?

Answer: _____

b) (1 pt) What is the value of K for the reaction?

Answer: _____

c) (3 pts) What is the percent yield of C?

Answer: _____

d) (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

4. (5 pts) A 0.168 L sample of oxygen is collected over water at 26.0°C. The pressure of the gas mixture is measured to be 737 mmHg. The vapour pressure of water at 26.0°C is 25.2 mmHg. In the mixture, what is the percent water vapour by *mass*?

Answer: _____

5. (4 pts) Dr. Fox's favourite single malt scotch whisky is *Lagavulin*, which is 43.0% ethanol (C_2H_5OH) by volume. While marking midterms, Dr. Fox drinks 35.0 mL of the scotch, of which 22.0% of the ethanol by mass is absorbed into her blood. If Dr. Fox has 6.60 L of blood, what concentration (in g/mL) of ethanol is in her blood? (*d* of ethanol = 0.789 g/mL)

Answer: _____

LAST NAME: _____

FIRST NAME: _____

Student Number: _____

CHM 1311 A
Midterm #2
Fall 2016

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.

Question	Points Possible	Points Earned	TA Initial
1	6		
2	10		
3	5		
4	4		
5	10		
TOTAL	35		

1. Short Answer Questions

a) (1 pt) A stovetop transfers 128 kJ of heat to a pot of boiling water. The mass of steam that escapes is _____.

b) (1.5 pts) The standard heat of formation of solid $Pb(NO_3)_2$ is –452 kJ. Write the chemical equation for the reaction to which this value applies (include phases).

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

KCl	**$NaOCl_2$**	**NH_4Br**
$Al_2(SO_4)_3$	**LiF**	**$CuNO_3$**

d) (0.5 pt) NH_3 is both an Arrhenius base and a Brønsted base. TRUE FALSE

e) (1 pt) For the reaction A (g) → 2 B (g), we observe that the rate of disappearance of A is constant as the reaction progresses. Therefore, for the reaction:

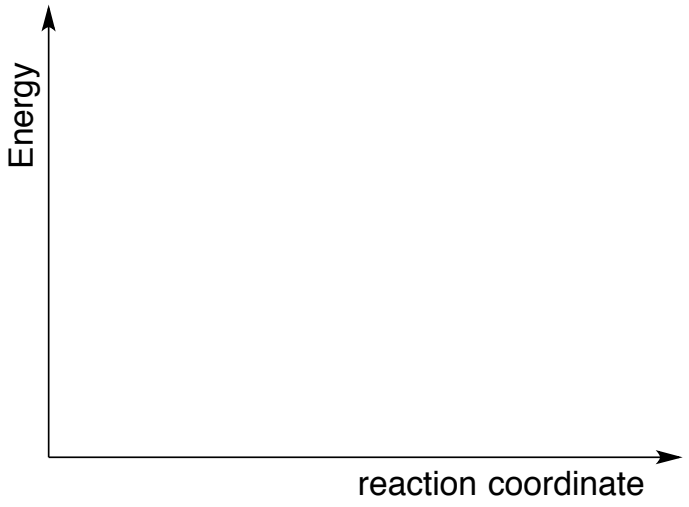
- **the graph of _____ versus time will be a linear plot**
- **the half-life will INCREASE DECREASE as $[A]_o$ decreases**

(1 pt) BONUS:

The overall exothermic chemical reaction

$$A + B \rightarrow C$$

follows a two-step mechanism, involving a fast step followed by a slow step. On the axes provided a right, draw a representative reaction profile for this process. Thoroughly label your diagram.



2. The reaction of NO_2 and CO to make NO and CO_2 is believed to occur via a two-step mechanism:

$$NO_2 + NO_2 \rightarrow NO + NO_3$$

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

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

b) (3 pts) The rate law is determined experimentally to be: rate = $k[NO_2]^2$. Is the proposed mechanism reasonable? Why or why not? What would be the rate-determining step?

c) (2 pts) When the initial concentration of NO_2 is 0.010 M, the initial rate of reaction is 5.5×10^{-6} M/s. Find the value of the rate constant, with the appropriate units.

d) (3 pts) What will be the concentration of NO_2 after 3.00 min if its initial concentration is 0.033 M?

3. (5 pts) The pH of an aqueous solution of HCN is measured to be 5.77. What was the initial concentration of HCN, in mmol/L?

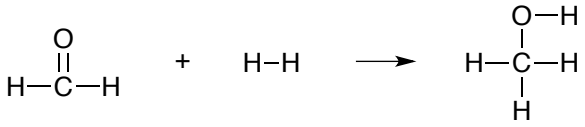
4. For the acid-base reaction below:

$$F^- + HN_3 \leftrightarrows$$

a) (2 pts) Add the expected products and label the acid, base, conjugate acid, and conjugate base.

b) (2 pts) Does the equilibrium favour the reactants or products? Justify your answer.

5. Consider the following hydrogenation reaction, which takes place entirely in the gas phase at 600 K:



Bond	Energy (kJ)	Bond	Energy (kJ)
C–C	345	C=C	615
C–H	415	O=O	495
O–H	460	C=O	750
C–O	360	H–H	435

a) (5 pts) Estimate the total internal energy change, in kJ, using bond energies.

b) (2 pts) Find the quantity of work associated with this reaction at 600 K, in kJ.

c) (1 pt) Find the enthalpy change associated with this reaction at 600 K, in kJ.

d) (2 pts) At right, draw a representative energy diagram for this reaction. Fully label your diagram, including: ΔE, E_1, E_2, q, and W.

Last Name: _____

First name: _____

Student Number: _____ **Seat Number:** _____

CHM 1311 A
Final Exam
December 2016

Professor: Dr. Fox

There are 17 pages in this exam. A periodic table, data tables, and a formula sheet are provided at the end. You may gently remove these pages and use them to cover your work. Any scratch work should be done on these pages or on the scrap paper provided.

Please show all work to receive partial credit.

You have 180 minutes to complete the exam.

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: _____

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) (2 pts) Find the overall redox reaction (acidic conditions) from these half-reactions:

$$Cu^{+} \rightarrow Cu^{2+}$$

$$BrO_3^{-} \rightarrow BrO_2^{-}$$

OVERALL: _____

b) (2 pts) 40.0 mL of 0.50 M HOCl is titrated with 0.50 M NaOH. The total volume and pH of solution at the half equivalence point are _____ and _____.

c) (1 pt) For a given reaction, the plot of lnk versus 1/T yields a slope of + 13.9 and a y-intercept of 2.6×10^6. Knowing this information, the reaction has:

$E_a > 0$ $\Delta H < 0$ $E_a < 0$ $\Delta H > 0$

d) (2 pts) Write the equilibrium constant expression for the following reaction, and choose the best means by which you could encourage the formation of hydrogen gas.

$C(s) + H_2O(g) \leftrightarrows CO(g) + H_2(g)$ $\Delta H^o = 211$ kJ

☐ Add steam and remove heat
☐ Increase volume and add heat
☐ Remove carbon monoxide and decrease volume
☐ Add hydrogen gas and increase volume

K =

e) (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 0.0106 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of effusion would be _____.

f) (0.5 pts) NH_3 is both an Arrhenius base and a Brønsted base. TRUE FALSE

g) (1.5 pts) Complete the following table:

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
Sn	102				+2

h) (2 pts) For a zero order reaction, the half-life _____ with increasing reactant concentration. For a second order reaction, the half-life _____ with increasing reactant concentration.

i) (2 pts) For the compounds listed below, circle those whose solubility will increase in acidic solution and underline those whose solubility will increase in basic solution.

PbS $NaNO_3$ BaF_2

$Zn(OH)_2$ $Ti(SO_4)_2$ $CaCl_2$

j) (1.5 pts) An endothermic contraction of a gas has a POSITIVE NEGATIVE value of W, a POSITIVE NEGATIVE value of q, and a POSITIVE NEGATIVE value of ΔE.

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

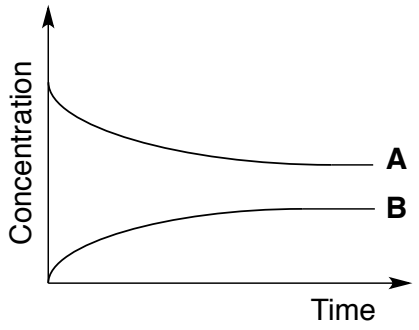
l) (1 pt) The expression which describes the heat of a reaction under all possible conditions is:

ΔE ΔH q_v q_p $\Delta E - W$

m) (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

n) (1 pt) The graph at right represents the concentrations as a function of time for the reaction A(g) ⇆ B(g). Which of the following statements is/are true?

- ☐ **K_P is equal to 1**
- ☐ **K_P is greater than 1**
- ☐ **K_P is less than 1**
- ☐ **K_P is equal to K_C**
- ☐ **The system never reaches equilibrium**



o) (1 pt) According to the Bohr Model, which of the following electronic transitions corresponds to the absorption of a photon with the shortest wavelength?

$n = 1 \rightarrow n = 3$ $n = 2 \rightarrow n = 3$

$n = 3 \rightarrow n = 1$ $n = 3 \rightarrow n = 2$

BONUS – 2 pts

The following is a hypothetical configuration for the ground state of a chromium atom. This configuration is incorrect because:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$$

- ☐ **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**

Give the correct ground state configuration of chromium: _____

2. Electrons in Atoms.

a) (3 pts) For the following sets of quantum numbers, give the subshell label, the allowed values of m_l and the number of orbitals in the subshell (the first row is an example).

n and l	subshell label	m_l values	number of orbitals
n = 1 and l = 0	1*s*	0	1
n = 3 and l = 1			
n = 5 and l = 2			

b) (3 pts) How many electrons can be described by each of the following sets of quantum numbers?

i. $n = 4, l = 2, m_l = 3$

ii. $n = 3, l = 2, m_l = -1, m_s = -\frac{1}{2}$

iii. $n = 4, l = 3$

c) (4 pts) Draw the orbital energy diagram for Fe^{2+} in the space below. What is the expected magnetism of this species?

3. Antifreeze is an aqueous solution containing 28.6% ethylene glycol ($C_2H_6O_2$) by mass. The density of the solution is 1.03 g/cm^3.

a) (3 pts) Calculate the molarity of this solution.

Answer: _____

b) (3 pts) Calculate the molality of this solution.

Answer: _____

c) (4 pts) If the molar heat capacity of ethylene glycol is 149.5 J/mol°C, how much heat (in J) is needed to raise the temperature of 1.00 L of antifreeze from 10.0°C to 25.0°C?

4. The following reaction, occurring in a sealed vessel, has a percent yield of 94.9%:

$$2NaN_3\ (s) \rightarrow 2\ Na\ (l) + 3\ N_2(g)$$

a) (8 pts) What volume of N_2, measured at 735 mmHg and 26.0°C, is produced when 75.0 g of sodium azide decomposes?

Answer: _____

b) (2 pts) After the reaction is complete, argon gas is added to the vessel until the final total pressure is 1000 mmHg. What is the mole fraction of nitrogen in the gas mixture?

Answer: _____

5. You are provided 500.0 mL of a 3.50 M solution of H_3PO_4, which you will use to prepare a buffer with pH = 2.10. Your TA gives you a jar of solid NaOH and a jar of solid Na_3PO_4. (For H_3PO_4, $K_{a1} = 7.5x10^{-3}$, $K_{a2} = 6.2x10^{-8}$, and $K_{a2} = 2.2x10^{-13}$)

a) (1 pt) Which component, NaOH or solid Na_3PO_4, will you need to make the buffer?

NaOH Na_3PO_4

b) (2 pts) The 2.50 L buffer has a total concentration of phosphate-containing species of 0.155 M. What volume of 3.50 M H_3PO_4 was required to make the buffer solution?

c) (4 pts) What mass of solid (chosen in part a) was required to make the buffer solution?

d) (3 pts) What will be the new pH of the buffer if 0.030 mol of NaOH is added to it?

6. 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 $[NO]_i = 6.00$ M and $[H_2]_i = 1.00 \times 10^{-4}$ M, the initial rate of reaction is 3.0×10^{-6} M/s. Find the value of the rate constant, with the appropriate units.

d) (3 pts) What will be $[H_2]$ after 5.00 s using the conditions from part c)? HINT: note the relative reactant concentrations!

7. Acids and Bases.

a) (4 pts) A student prepares a 0.120 M solution of an unknown monoprotic acid. At equilibrium, she measures the pH to be 2.561. Identify the acid.

b) (3 pts) Vinegar is a dilute aqueous solution of acetic acid. The legal minimum acetic acid content of vinegar is 4.0% by mass. Dr. Fox takes a 5.00 mL sample of President's Choice brand vinegar (d = 1.01 g/mL) and titrates it to completion with 39.55 mL of 0.1000 M NaOH. Does the sample exceed the legal minimum content?

c) (4 pts) What would be the pH at the equivalence point of the titration in part (b)? You may assume that volumes are additive.

8. Wastewater resulting from metal processing is polluted with cadmium ions, Cd^{2+}, which must be removed before the water may be disposed. In one method, the water is treated with solutions of concentrated sodium hydroxide. Suppose 1.00×10^2 L of wastewater containing 1.2×10^{-5} M Cd^{2+} is treated with 1.0 L of 6.0 M NaOH solution.

a) (1 pt) What is the insoluble solid that precipitates out? _____

b) (6 pts) What is the residual concentration of aqueous cadmium ion after treatment?

c) (3 pts) What is the mass of the solid that precipitates out?

9. 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) (5 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?

CHM1311 A **Name :** _____

TWO STAGE DGD QUIZ (MONDAY)

October 3 2016

STAGE 1 : INDIVIDUAL RESPONSES (30 min)

1. **(6 pts) Elemental phosphorus, P_4, reacts vigorously with molecular oxygen to give P_4O_{10}. Calculate the mass of P_4O_{10} that can be prepared from 3.75 g of P_4 and 6.55 g of O_2. Identify the excess reactant and calculate how many grams of it remains at the end of the reaction.**

THIS IS OLMSTED SUGGESTED PROBLEM 1.75

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

	P_4 + 5 O_2 → P_4O_{10}		
mass (g)	3.75	6.55	
molar mass (g/mol)	123.88	32.00	283.88
moles	0.03027	0.2047	

Now, we determine the theoretical amount of product formed from each reactant:

$$\text{? theo. mol } P_4O_{10} \text{ from } P_4 = 0.03027 \text{ mol } P_4 \times \frac{1 \text{ mol } P_4O_{10}}{1 \text{ mol } P_4} = 0.03027 \text{ mol}$$

$$\text{? theo. mol } P_4O_{10} \text{ from } O_2 = 0.2047 \text{ mol } O_2 \times \frac{1 \text{ mol } P_4O_{10}}{5 \text{ mol } O_2} = 0.0494 \text{ mol}$$

Therefore, P_4 is the limiting reagent and O_2 is present in excess.

$$\text{? theo. g } P_4O_{10} = 0.03027 \text{ mol } P_4O_{10} \times \frac{283.88 \text{ g } P_4O_{10}}{1 \text{ mol } P_4O_{10}} = 8.6 \text{ g}$$

$$\text{? mol } O_2 \text{ reacted} = 0.03027 \text{ mol } P_4O_{10} \times \frac{5 \text{ mol } O_2}{1 \text{ mol } P_4O_{10}} = 0.1514 \text{ mol}$$

$$\text{? g } O_2 \text{ leftover} = (0.2047 \text{ mol} - 0.1514 \text{ mol}) \times \frac{32.00 \text{ g } O_2}{1 \text{ mol } O_2} = 1.71 \text{ g}$$

Mass of P_4O_{10} = ____8.6 g_____ **Excess reactant and mass =** ____O_2, 1.71 g_____

2. (4 pts) What is the mole fraction of ethyl alcohol (C_2H_6O, density = 0.79 g/ml) in water for a solution made from equal volumes of each liquid?

THIS QUESTION WAS TAKEN FROM ASSIGNMENT #2
AND WAS COVERED IN THE SEPT 26 DGD (YOU CAN WATCH THE VIDEO)

Let's assume we have 100 mL of each liquid. We can create a table using all the available data:

	C_2H_6O	H_2O
V (mL)	100	100
d (g/mL)	0.79	1.00
mass (g)	79	100
molar mass (g/mol)	46.07	18.02
mol	1.72	5.55

The total number of moles = 1.72 + 5.55 = 7.27 mol

$$\therefore \chi_{C_2H_6O} = \frac{1.72 \text{ mol}}{7.27 \text{ mol}} = 0.24$$

Mole fraction = _____0.24_____

3. (5 pts) Balance the following half-reaction in basic solution. No phases required.

$$Se + Cr(OH)_3 \rightarrow SeO_3^{2-} + Cr$$

THIS QUESTION WAS TAKEN FROM ASSIGNMENT #2

The balanced half reactions are:

$$6\ OH^- + Se \rightarrow SeO_3^{2-} + 3\ H_2O + 4e^-$$

$$3e^- + Cr(OH)_3 \rightarrow Cr + 3\ OH^-$$

Using the lowest common denominator (12), adding the two half reactions and simplifying gives the final overall balanced redox reaction:

$$6\ OH^- + 3\ Se + 4\ Cr(OH)_3 \rightarrow 3\ SeO_3^{2-} + 9\ H_2O + 4\ Cr$$

1. Short Answer Questions

a) (1.5 pts) In the following redox reaction, label the oxidation states of each element and circle the oxidizing agent:

$$\underset{-2\ +1}{N_2H_4\,(aq)} + \underset{+2}{2\,Zn^{2+}\,(aq)} + \underset{-2\ +1}{4OH^-\,(aq)} \rightarrow \underset{0}{N_2\,(g)} + \underset{0}{2\,Zn\,(s)} + \underset{+1\ -2}{4\,H_2O\,(l)}$$

b) (0.5 pt) In the reaction: N_2O_4 (g) ⇆ 2 NO_2 (g) (ΔH = 57.2 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. 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

c) (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

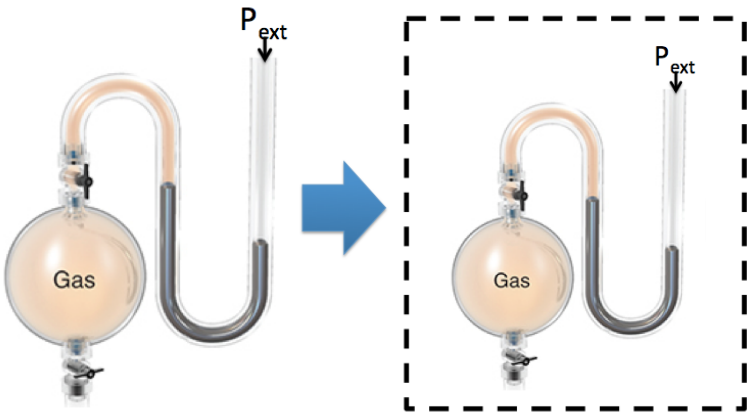
d) (1 pt) Toothpaste contains 0.24% m/v sodium fluoride. This concentration expressed in mol/L is: 0.057 mol/L

e) (1.5 pts) Complete the following table:

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
As	70	33	30	37	+3

(1 pt) BONUS:

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



2. Complete combustion of a 1.505 g sample of an unknown gaseous compound (consisting of C, H, and S) yields 3.149 g of CO_2, 0.645 g of H_2O, and some SO_2.

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

THIS QUESTION IS A MODIFIED VERSION OF AN EXAMPLE IN THE NOTES

$$?\,mol\,C = 3.149\,g\,CO_2 \times \frac{mol\;CO_2}{44.01\,g\,CO_2} \times \frac{1\,mol\,C}{1\,mol\,CO_2} = 0.07155\,mol\,C$$

$$?\,mol\,H = 0.645\,g\,H_2O \times \frac{mol\,H_2O}{18.02\,g\,H_2O} \times \frac{2\,mol\,H}{1\,mol\,H_2O} = 0.07159\,mol$$

$$?\,g\,C = 0.07155\,mol\,C \times \frac{12.011\,g\,C}{mol\,C} = 0.859\,g\,C$$

$$?\,g\,H = 0.07159\,mol\,H \times \frac{1.008\,g\,H}{mol\,H} = 0.072\,g\,H$$

$$?\,mol\,S = (1.505\,g - 0.859\,g - 0.072\,g) \times \frac{mol\,S}{32.066\,g\,S} = 0.0179\,mol\,S$$

C = 0.07155 mol **H =** 0.07159 mol **S =** 0.0179 mol

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

$$C_{\frac{0.07155}{0.0179}}H_{\frac{0.07159}{0.0179}}S_{\frac{0.0179}{0.0179}} = C_4H_4S$$

c) (3 pts) A 0.178 g sample of the gas in a 25.0 mL container has a pressure of 1.055 bar at 300.0 K. What is the molar mass of the unknown compound?

$$?\,mol\,gas = \frac{PV}{RT} = \frac{(1.055\,bar)(0.0250\,L)}{(0.083145\,L \bullet bar \bullet mol^{-1} \bullet K^{-1})(300.0K)} = 0.00106\,mol$$

$$\therefore ?\frac{g}{mol} = \frac{0.178\,g}{0.00106\,mol} = 168\,g/mol$$

Answer: 168 g/mol

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

$$Stoichiometric\;factor = \frac{MF\;mass}{EF\;mass} = \frac{168}{84} = 2$$

$C_8H_8S_2$

3. 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 A MODIFIED QUESTION FROM MIDTERM#2 2015

a) (5 pts) What is the total pressure in the flask at equilibrium?

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

$$= 0.154\text{ bar}$$

	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

$P_{TOT} = 0.246\text{ bar} + 0.092\text{ bar} + 0.154\text{ bar} = 0.492\text{ bar}$

Answer: ____0.492 bar_____

b) (1 pt) What is the value of K for the reaction?

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

Answer: _____74.0_____

c) (3 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.

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

Answer: _____77%_____

d) (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

4. (5 pts) A 0.168 L sample of oxygen is collected over water at 26.0°C. The pressure of the gas mixture is measured to be 737 mmHg. The vapour pressure of water at 26.0°C is 25.2 mmHg. In the mixture, what is the percent water vapour by *mass*?

THIS QUESTION WAS COVERED IN THE SEPT 26 DGD

$$P_{H_2O} = 25.2mmHg \times \frac{1.01325bar}{760mmHg} = 0.0336\ bar$$

$$P_{O_2} = (737mmHg - 25.2mmHg) \times \frac{1.01325bar}{760mmHg} = 0.949\ bar$$

$$?\ g\ H_2O = \frac{(0.0336\ bar)(0.168L)}{(0.083145bar \bullet L \bullet mol^{-1} \bullet K^{-1})(299K)} \times \frac{18.02\ g}{mol} = 0.00409\ g$$

$$?\ g\ O_2 = \frac{(0.949\ bar)(0.168L)}{(0.083145bar \bullet L \bullet mol^{-1} \bullet K^{-1})(299K)} \times \frac{32.00\ g}{mol} = 0.205\ g$$

$$\%mass = \frac{0.00409\ g}{0.00409\ g + 0.205\ g} \times 100\% = 1.95\%$$

Answer: 1.95%

5. (4 pts) Dr. Fox's favourite single malt scotch whisky is *Lagavulin*, which is 43.0% ethanol (C_2H_5OH) by volume. While marking midterms, Dr. Fox drinks 35.0 mL of the scotch, of which 22.0% of the ethanol by mass is absorbed into her blood. If Dr. Fox has 6.60 L of blood, what concentration (in g/mL) of ethanol is in her blood? (*d* of ethanol = 0.789 g/mL)

THIS QUESTION WAS TAKEN FROM MIDTERM #1 2013

Let "EtOH" represent ethanol.

$$?\text{ g EtOH absorbed} = 35\text{ mL scotch} \times \frac{43\text{ mL EtOH}}{100\text{ mL scotch}} \times \frac{0.789\text{ g EtOH}}{\text{mL EtOH}} \times \frac{22\text{ g EtOH absorbed}}{100\text{ g EtOH consumed}}$$

$$= 2.61\text{ g}$$

$$\frac{?\text{ g EtOH absorbed}}{\text{mL blood}} = \frac{2.61\text{ g EtOH absorbed}}{6.6\text{ L blood}} \times \frac{1\text{ L}}{1000\text{ mL}}$$

$$= 4.0x10^{-4}\text{ g/mL}$$

Answer: $4.0x10^{-4}$ g/mL

1. Short Answer Questions

a) (1 pt) A stovetop transfers 128 kJ of heat to a pot of boiling water. The mass of steam that escapes is 57 g.

b) (1.5 pts) The standard heat of formation of solid $Pb(NO_3)_2$ is –452 kJ. Write the chemical equation for the reaction to which this value applies (include phases).

$$Pb\,(s) + N_2\,(g) + 3\,O_2\,(g) \rightarrow Pb(NO_3)_2\,(s)$$

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

KCl	$NaOCl_2$	NH_4Br
$Al_2(SO_4)_3$	LiF	$CuNO_3$

d) (0.5 pt) NH_3 is both an Arrhenius base and a Brønsted base. TRUE FALSE

e) (1 pt) For the reaction A (g) → 2 B (g), we observe that the rate of disappearance of A is constant as the reaction progresses. Therefore, for the reaction:

if rate = constant, it must be ZERO ORDER, so:

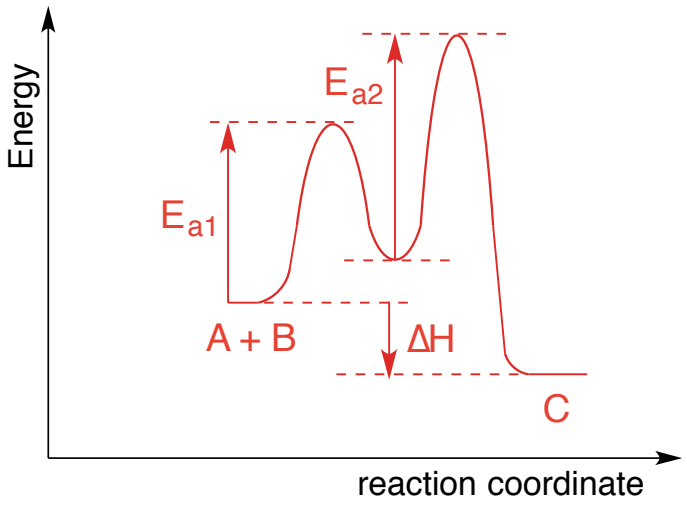
- the graph of [A] versus time will be a linear plot
- the half-life will INCREASE DECREASE as $[A]_o$ decreases

(1 pt) BONUS:

The overall exothermic chemical reaction

$$A + B \rightarrow C$$

follows a two-step mechanism, involving a fast step followed by a slow step. On the axes provided a right, draw a representative reaction profile for this process. Thoroughly label your diagram.



2. The reaction of NO_2 and CO to make NO and CO_2 is believed to occur via a two-step mechanism:

$$NO_2 + NO_2 \rightarrow NO + NO_3$$

$$NO_3 + CO \rightarrow NO_2 + CO_2$$

This question is from the 2012 Final Exam

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

Overall reaction = $NO_2 + CO \rightarrow NO + CO_2$

Intermediate = NO_3

b) (3 pts) The rate law is determined experimentally to be: rate = $k[NO_2]^2$. Is the proposed mechanism reasonable? Why or why not? What would be the rate-determining step?

Rate 1 = $k_1[NO_2]^2$

Rate 2 = $k_2[NO_3][CO]$

So far, YES, the mechanism is reasonable, because the experimentally observed rate law matches the expected rate law of one of the steps. This means step one is the RDS.

c) (2 pts) When the initial concentration of NO_2 is 0.010 M, the initial rate of reaction is 5.5×10^{-6} M/s. Find the value of the rate constant, with the appropriate units.

$$\text{rate} = k[NO_2]^2$$

$$\therefore k = \frac{\text{rate}}{[NO_2]^2} = \frac{5.5 \times 10^{-6}\ \text{M} \cdot \text{s}^{-1}}{(0.010\text{M})^2} = 0.055\ \text{M}^{-1} \cdot \text{s}^{-1}$$

d) (3 pts) What will be the concentration of NO_2 after 3.00 min if its initial concentration is 0.033 M?

$$\frac{1}{[NO_2]_t} = \frac{1}{[NO_2]_o} + kt$$

$$\frac{1}{[NO_2]_t} = \frac{1}{0.033\ \text{M}} + (0.055\ \text{M}^{-1} \cdot \text{s}^{-1})(180\ \text{s}) = 40.2\ \text{M}^{-1}$$

$$\therefore [NO_2]_t = \frac{1}{40.2\ \text{M}^{-1}} = 0.025\ \text{M}$$

3. (5 pts) The pH of an aqueous solution of HCN is measured to be 5.77. What was the initial concentration of HCN, in mmol/L?

This is similar to a question covered in the NOV 14 DGD

	HCN	+ H_2O ⇆	H_3O^+	+ CN^-
I	$[HCN]_o$	-	0	0
C	$-x$	-	$+x$	$+x$
E	$[HCN]_o - x$	-	x	x

$$[H_3O^+] = 10^{-5.77} = 1.70\times10^{-6}\ \text{M} = x$$

$$K_a = \frac{[H_3O^+][CN^-]}{[HCN]}$$

$$6.2\times10^{-10} = \frac{x^2}{[HCN]_o - x} = \frac{(1.70\times10^{-6})^2}{[HCN]_o - 1.70\times10^{-6}}$$

$$6.2\times10^{-10}[HCN]_o - 1.054\times10^{-15} = 2.89\times10^{-12}$$

$$\therefore [HCN]_o = 4.66\times10^{-3}\ \text{M} = 4.66\ \text{mM}$$

(Note: you can also solve this by making the assumption "x is small"; if you did, you'll have to verify that assumption.)

4. For the acid-base reaction below:

F^-	+	HN_3	⇆	HF	+	N_3^-
BASE		ACID		CONJ. ACID		CONJ. BASE

This question is a modified in-class Echo360 question

a) (2 pts) Add the expected products and label the acid, base, conjugate acid, and conjugate base.

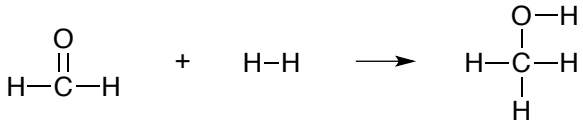
b) (2 pts) Does the equilibrium favour the reactants or products? Justify your answer.

K_a of HN_3 is 1.9×10^{-5}

K_a of HF is 6.6×10^{-4}

Therefore, HF is the stronger acid (better proton donor), and the equilibrium goes right to left, favouring REACTANTS.

5. Consider the following hydrogenation reaction, which takes place entirely in the gas phase at 600 K:



Bond	Energy (kJ)	Bond	Energy (kJ)
C–C	345	C=C	615
C–H	415	O=O	495
O–H	460	C=O	750
C–O	360	H–H	435

This is a new question, made by combining 2 in-class questions

a) (5 pts) Estimate the total internal energy change, in kJ, using bond energies.

BROKEN:		
1 x C=O	1 x 750 kJ	750 kJ
1 x H-H	1 x 435 kJ	435 kJ
	TOTAL	+ 1185 kJ
FORMED:		
1 x C–O	1 x 360 kJ	360 kJ
1 x C–H	1 x 415 kJ	415 kJ
1 x O–H	1 x 460 kJ	460 kJ
	TOTAL	–1235 kJ

$\Delta E = +1185\ kJ + (-1235\ kJ) = -50\ kJ$

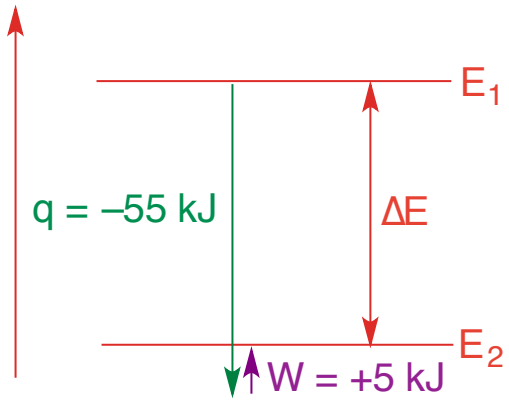
b) (2 pts) Find the quantity of work associated with this reaction at 600 K, in kJ.

$$W = -\Delta nRT = -(-1\ mol)(8.3145\ J/mol \cdot K)(600K) = +4573\ J = +4.6\ kJ$$

c) (1 pt) Find the enthalpy change associated with this reaction at 600 K, in kJ.

$\Delta E = q + w = \Delta H + W$
$\Delta H = \Delta E - W = -50\ kJ - (4.6\ kJ) = -55\ kJ$

d) (2 pts) At right, draw a representative energy diagram for this reaction. Fully label your diagram, including: ΔE, E_1, E_2, q, and W.



1. Short Answer Questions.

a) (2 pts) Find the overall redox reaction (acidic conditions) from these half-reactions:

$$2\,Cu^{+} \rightarrow 2\,Cu^{2+} + 2e^{-}$$

$$2e^{-} + 2\,H^{+} + BrO_3^{-} \rightarrow BrO_2^{-} + H_2O$$

OVERALL: $2\,Cu^{+} + 2\,H^{+} + BrO_3^{-} \rightarrow 2\,Cu^{2+} + BrO_2^{-} + H_2O$

b) (2 pts) 40.0 mL of 0.50 M HOCl is titrated with 0.50 M NaOH. The total volume and pH of solution at the half equivalence point are ___60.0 mL_____ and __7.54___.

c) (1 pt) For a given reaction, the plot of lnk versus 1/T yields a slope of + 13.9 and a y-intercept of 2.6×10^6. Knowing this information, the reaction has:

$E_a > 0$ $\Delta H < 0$ $E_a < 0$ $\Delta H > 0$

d) (2 pts) Write the equilibrium constant expression for the following reaction, and choose the best means by which you could encourage the formation of hydrogen gas.

$C(s) + H_2O(g) \leftrightarrows CO(g) + H_2(g)$ $\Delta H^{o} = 211$ kJ

- ☐ Add steam and remove heat
- ☐ Increase volume and add heat
- ☐ Remove carbon monoxide and decrease volume
- ☐ Add hydrogen gas and increase volume

K = $\dfrac{P_{CO} \times P_{H_2}}{P_{H_2O}}$

e) (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 0.0106 mol/hr. If the same balloon is refilled with argon at the same pressure and temperature, its rate of effusion would be ____0.0075 mol/hr_____.

f) (0.5 pts) NH_3 is both an Arrhenius base and a Brønsted base. TRUE FALSE

g) (1.5 pts) Complete the following table:

Element	Mass Number	Number of protons	Number of electrons	Number of neutrons	Charge
Sn	102	50	48	52	+2

h) (2 pts) For a zero order reaction, the half-life _____increases_____ with increasing reactant concentration. For a second order reaction, the half-life _____decreases_____ with increasing reactant concentration.

i) (2 pts) For the compounds listed below, circle those whose solubility will increase in acidic solution and underline those whose solubility will increase in basic solution.

PbS $NaNO_3$ BaF_2

$Zn(OH)_2$ $Ti(SO_4)_2$ $CaCl_2$

j) (1.5 pts) An endothermic contraction of a gas has a POSITIVE NEGATIVE value of W, a POSITIVE NEGATIVE value of q, and a POSITIVE NEGATIVE value of ΔE.

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

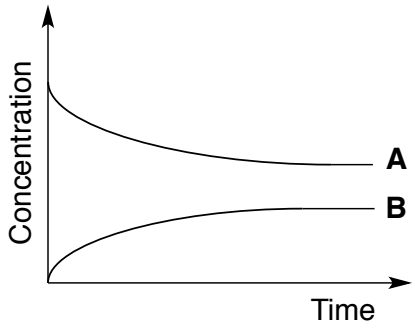
l) (1 pt) The expression which describes the heat of a reaction under all possible conditions is:

ΔE ΔH q_v q_p ΔE – W

m) (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

n) (1 pt) The graph at right represents the concentrations as a function of time for the reaction A(g) ⇆ B(g). Which of the following statements is/are true?

- ☐ K_P is equal to 1
- ☐ K_P is greater than 1
- ☐ K_P is less than 1
- ☐ K_P is equal to K_C
- ☐ The system never reaches equilibrium



o) (1 pt) According to the Bohr Model, which of the following electronic transitions corresponds to the absorption of a photon with the shortest wavelength?

$n = 1 \rightarrow n = 3$ $n = 2 \rightarrow n = 3$

$n = 3 \rightarrow n = 1$ $n = 3 \rightarrow n = 2$

BONUS – 2 pts

The following is a hypothetical configuration for the ground state of a chromium atom. This configuration is incorrect because:

$$1s^2 2s^2 2p^6 3s^2 3p^6 4s^2 3d^4$$

- ☐ 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

Give the correct ground state configuration of chromium: _____$1s^2 2s^2 2p^6 3s^2 3p^6 4s^1 3d^5$___

2. Electrons in Atoms.

a) (3 pts) For the following sets of quantum numbers, give the subshell label, the allowed values of m_l and the number of orbitals in the subshell (the first row is an example).

n and l	subshell label	m_l values	number of orbitals
n = 1 and l = 0	1*s*	0	1
n = 3 and l = 1	3p	-1, 0, 1	3
n = 5 and l = 2	5d	-2, -1, 0, 1, 2	5

b) (3 pts) How many electrons can be described by each of the following sets of quantum numbers?

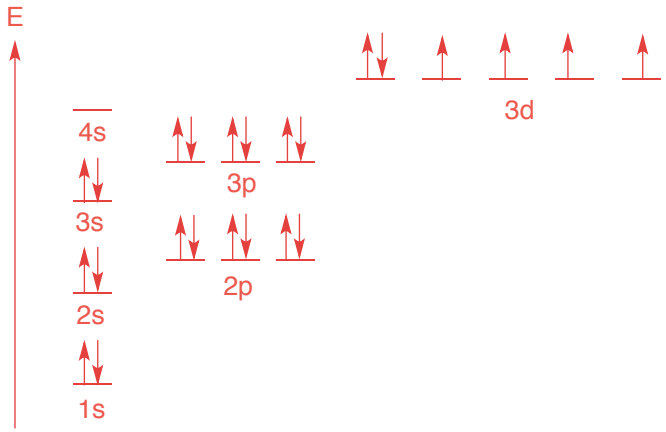
i. $n = 4, l = 2, m_l = 3$ — **0** — **(m_l cannot be +3)**

ii. $n = 3, l = 2, m_l = -1, m_s = -½$ — **1** — **(this is an e⁻ in a 3d orbital)**

iii. $n = 4, l = 3$ — **14** — **(these are the 4f electrions)**

c) (4 pts) Draw the orbital energy diagram for Fe^{2+} in the space below. What is the expected magnetism of this species?

PARAMAGNETIC.



(the unpaired electrons in 3d can also be spin down instead)

3. Antifreeze is an aqueous solution containing 28.6% ethylene glycol ($C_2H_6O_2$) by mass. The density of the solution is 1.03 g/cm³.

a) (3 pts) Calculate the molarity of this solution.

Say we have 100 g of antifreeze:

$$?\ \text{mol}\ C_2H_6O_2 = 100\ \text{g antifreeze} \times \frac{28.6\ \text{g}\ C_2H_6O_2}{100\ \text{g antifreeze}} \times \frac{\text{mol}\ C_2H_6O_2}{62.0\ \text{g}\ C_2H_6O_2} = 0.461\ \text{mol}$$

$$?\ \text{L antifreeze} = 100\ \text{g antifreeze} \times \frac{\text{mL antifreeze}}{1.01\ \text{g antifreeze}} \times \frac{\text{L}}{1000\ \text{mL}} = 0.0990\ \text{L}$$

$$\therefore \text{molarity} = \frac{0.461\ \text{mol}}{0.0990\ \text{L}} = 4.65\ \text{mol/L}$$

Answer: _____**4.65 M**_____

b) (3 pts) Calculate the molality of this solution.

$$?\ \text{kg}\ H_2O = (100\ \text{g antifreeze} - 28.6\ \text{g}\ C_2H_6O_2) \times \frac{\text{kg}}{1000\ \text{g}} = 0.0714\ \text{kg}$$

$$\therefore \text{molality} = \frac{0.461\ \text{mol}}{0.0714\ \text{kg}} = 6.46\ \text{mol/kg}$$

Answer: _____**6.46 *m***_____

c) (4 pts) If the molar heat capacity of ethylene glycol is 149.5 J/mol°C, how much heat (in J) is needed to raise the temperature of 1.00 L of antifreeze from 10.0°C to 25.0°C?

$$?\ \text{g antifreeze} = 1.00\ \text{L antifreeze} \times \frac{1000\ \text{mL}}{\text{L}} \times \frac{1.01\ \text{g antifreeze}}{\text{mL antifreeze}} = 1010\ \text{g antifreeze}$$

$$?\ \text{mol}\ C_2H_6O_2 = 1010\ \text{g antifreeze} \times \frac{28.6\ \text{g}\ C_2H_6O_2}{100\ \text{g antifreeze}} \times \frac{\text{mol}\ C_2H_6O_2}{62.0\ \text{g}\ C_2H_6O_2} = 4.66\ \text{mol}$$

$$\text{q for}\ C_2H_6O_2 = mc\Delta T = (4.66\ \text{mol})(149.5\ \text{J/mol°C})(25.0°\text{C} - 10.0°\text{C}) = 1.045 \times 10^4\ \text{J}$$

$$?\ \text{g}\ H_2O = 1010\ \text{g antifreeze} \times \frac{(100 - 28.6)\ \text{g}\ H_2O}{100\ \text{g antifreeze}} = 721.1\ \text{g}\ H_2O$$

$$\text{q for}\ H_2O = mc\Delta T = (721.1\ \text{g})(4.184\ \text{J/g°C})(25.0°\text{C} - 10.0°\text{C}) = 4.526 \times 10^4\ \text{J}$$

$$\therefore q_{\text{total}} = (\text{q for}\ C_2H_6O_2) + (\text{q for}\ H_2O) = 1.045 \times 10^4\ \text{J} + 1.526 \times 10^4\ \text{J} = 5.57 \times 10^4\ \text{J}$$

4. The following reaction, occurring in a sealed vessel, has a percent yield of 94.9%:

$$2NaN_3\,(s) \rightarrow 2\,Na\,(l) + 3\,N_2(g)$$

a) (8 pts) What volume of N_2, measured at 735 mmHg and 26.0°C, is produced when 75.0 g of sodium azide decomposes?

$$\text{? theoretical mol } N_2 = 70\text{ g } NaN_3 \times \frac{\text{mol } NaN_3}{65.0\text{ g } NaN_3} \times \frac{3\text{ mol } N_2}{2\text{ mol } NaN_3} = 1.730\text{ mol}$$

$$\text{? actual mol } N_2 = 1.730\text{ mol} \times 0.949 = 1.642\text{ mol}$$

$$P = 735\text{ mm Hg} \times \frac{1\text{ atm}}{760\text{ atm}} = 0.967\text{ atm}$$

$$T = 26.0^{o}\text{C} + 273.15 = 299.15\text{ K}$$

$$V = \frac{nRT}{P} = \frac{(1.730\text{ mol})(0.08206\text{ L}\cdot\text{atm/mol}\cdot\text{K})(299.15\text{ K})}{(0.967\text{ atm})} = 41.7\text{ L}$$

Answer: _____41.7 L_____

b) (2 pts) After the reaction is complete, argon gas is added to the vessel until the final total pressure is 1000 mmHg. What is the mole fraction of nitrogen in the gas mixture?

$$P_{N_2} = 735\text{ mm Hg}$$

$$P_{total} = 1000\text{ mm Hg}$$

$$P_{N_2} = \chi_{N_2} \times P_{total}$$

$$\therefore \chi_{N_2} = \frac{P_{N_2}}{P_{total}} = \frac{735\text{ mmHg}}{1000\text{ mmHg}} = 0.735$$

Answer: _____0.735_____

5. You are provided 500.0 mL of a 3.50 M solution of H_3PO_4, which you will use to prepare a buffer with pH = 2.10. Your TA gives you a jar of solid NaOH and a jar of solid Na_3PO_4. (For H_3PO_4, $K_{a1} = 7.5\text{x}10^{-3}$, $K_{a2} = 6.2\text{x}10^{-8}$, and $K_{a2} = 2.2\text{x}10^{-13}$)

a) (1 pt) Which component, NaOH or solid Na_3PO_4, will you need to make the buffer?

NaOH Na_3PO_4

(this is because we want the conjugate acid-base pair to be $H_3PO_4/H_2PO_4^-$, since its pKa, 2.12, most closely matches the desired pH. Adding NaOH to the H_3PO_4 solution will convert some of the acid to its conjugate base).

b) (2 pts) The 2.50 L buffer has a total concentration of phosphate-containing species of 0.155 M. What volume of 3.50 M H_3PO_4 was required to make the buffer solution?

$V_1 = (C_2V_2)/C_1 = (0.155\ M \times 2.50\ L)/(3.50\ M) = 0.111\ L$

c) (4 pts) What mass of solid (chosen in part a) was required to make the buffer solution?

Let $[HA] = H_3PO_4$ and $[A^-] = H_2PO_4^-$:

$$[HA] + [A^-] = 0.155\ M$$
$$\therefore [A^-] = 0.155\ M - [HA]$$
$$pH = pKa + \log\frac{[A^-]}{[HA]}$$
$$2.10 = 2.12 + \log\frac{0.155 - [HA]}{[HA]}$$
$$\therefore [HA] = 0.0793\ M$$
$$[A^-] = 0.155\ M - 0.0793\ M = 0.0757\ M$$

Since all of the A^- present came from the titration of HA with OH^-:

$$\text{mol } OH^- \text{ added} = \text{mol } A^- \text{ present} = 2.50\ L \times \frac{0.0757\ \text{mol}}{L} = 0.18925\ \text{mol}$$
$$?\ \text{g NaOH} = 0.18925\ \text{mol } OH^- \times \frac{1\ \text{mol NaOH}}{1\ \text{mol } OH^-} \times \frac{40.0\ \text{g NaOH}}{\text{mol NaOH}} = 7.57\ \text{g}$$

d) (3 pts) What will be the new pH of the buffer if 0.030 mol of NaOH is added to it?

mol HA = (0.0793 mol/L)(2.50 L) = 0.19825 mol

	HA + OH^- →	A^- + H_2O		
B	0.19825	-	0.1825	-
A	-	0.030	-	-
M	–0.030	–0.030	+0.030	-
A	0.16825	0	0.21925	

$$pH = pKa + \log\frac{[A^-]}{[HA]}$$
$$pH = 2.12 + \log\frac{0.21925}{0.16825}$$
$$= 2.23$$

6. Consider the following three-step mechanism:

$$2\ NO \leftrightarrows N_2O_2 \quad \text{(fast)}$$
$$N_2O_2 + H_2 \rightarrow N_2O + H_2O \quad \text{(slow)}$$
$$\text{(fast)}$$

$$N_2O + H_2 \rightarrow N_2 + H_2O$$

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:

$$\text{rate} = k_2[N_2O_2][H_2]$$
$$k_1[NO]^2 = k_{-1}[N_2O_2]$$
$$\therefore [N_2O_2] = \frac{k_1}{k_{-1}}[NO]^2$$
$$\therefore \text{rate} = \frac{k_1 k_2}{k_{-1}}[NO]^2[H_2] = k_{obs}[NO]^2[H_2]$$

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

c) (2 pts) When $[NO]_i$ = 6.00 M and $[H_2]_i = 1.00\times10^{-4}$ M, the initial rate of reaction is 3.0×10^{-6} 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 5.00 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:

$$\text{rate} = k[NO]^2[H_2]$$
$$k' = k[NO]^2 = (8.33\times10^{-4}\ \text{M}^{-2}\cdot\text{s}^{-1})(6.00\ \text{M})^2 = 0.030\ \text{s}^{-1}$$
$$\therefore \ln[H_2]_t = \ln[H_2]_i - k't = \ln(1.0\times10^{-4}\ \text{M}) - (0.030\ \text{s}^{-1})(5.00\ \text{s}) = -9.36$$
$$\therefore [H_2]_t = e^{-9.36} = 8.6\times10^{-5}\ \text{M}$$

7. Acids and Bases.

a) (4 pts) A student prepares a 0.120 M solution of an unknown monoprotic acid. At equilibrium, she measures the pH to be 2.561. Identify the acid.

$[H_3O^+] = 10^{-pH} = 10^{-2.561} = 0.00275$ M

	HA	+	H_2O ⇆	H_3O^+	+	A^-
I	0.120	-	0	0		
C	–0.00275	-	+0.00275	+0.00275		
E	0.11725	-	0.00275	0.00275		

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

$$K_a = \frac{(0.00275)^2}{(0.11725)} = 6.4 \times 10^{-5}$$

This value is closest to BENZOIC ACID.

b) (3 pts) Vinegar is a dilute aqueous solution of acetic acid. The legal minimum acetic acid content of vinegar is 4.0% by mass. Dr. Fox takes a 5.00 mL sample of President's Choice brand vinegar (d = 1.01 g/mL) and titrates it to completion with 39.55 mL of 0.1000 M NaOH. Does the sample exceed the legal minimum content?

$$\text{mol } CH_3COOH = 0.03955 \text{ L NaOH} \times \frac{0.1000 \text{ mol NaOH}}{\text{L}} \times \frac{1 \text{ mol } CH_3COOH}{1 \text{ mol NaOH}} = 0.003955 \text{ mol}$$

$$\text{? g } CH_3COOH = 0.003955 \text{ mol } CH_3COOH \times \frac{40.0 \text{ g } CH_3COOH}{\text{mol } CH_3COOH} = 0.2373 \text{ g}$$

$$\text{? g vinegar} = 5.00 \text{ mL} \times \frac{1.01 \text{ g}}{\text{mL}} = 5.05 \text{ g}$$

$$\therefore \%CH_3COOH = \frac{0.2373 \text{ g}}{5.05 \text{ g}} \times 100\% = 4.7\%$$

c) (4 pts) What would be the pH at the equivalence point of the titration in part (b)? You may assume that volumes are additive.

At the equivalence point, all of the CH_3COOH has been converted into CH_3COO^-, the conjugate base, which hydrolyzes to give OH^-:

$$[CH_3COO^-] = \frac{0.003955 \text{ mol}}{0.00500 \text{ L} + 0.03955 \text{ L}} = 0.08877 \text{ M}$$

	A^-	+	H_2O ⇆	HA	+	OH^-
I	0.08877	-	0	0		
C	$-x$	-	$+x$	$+x$		
E	$0.08877 - x$	-	x	x		

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

$$\frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.08877 - x}$$

$$\therefore x = [OH^-] = 7.0 \times 10^{-6} \text{ M} \quad \text{(passes assumption)}$$

$$\therefore pOH = -\log(7.0 \times 10^{-6}) = 5.15$$

$$\therefore pH = 14 - 5.15 = 8.85$$

8. Wastewater resulting from metal processing is polluted with cadmium ions, Cd^{2+}, which must be removed before the water may be disposed. In one method, the water is treated with solutions of concentrated sodium hydroxide. Suppose 1.00 x 10^2 L of wastewater containing 1.2 x 10^{-5} M Cd^{2+} is treated with 1.0 L of 6.0 M NaOH solution.

a) (1 pt) What is the insoluble solid that precipitates out? ____$Cd(OH)_2$_____

b) (6 pts) What is the residual concentration of aqueous cadmium ion after treatment?

$$\text{mol } Cd^{2+} = 100 \text{ L} \times \frac{1.2 \times 10^{-5} \text{ mol}}{\text{L}} = 0.0012 \text{ mol}$$

$$\text{mol } OH^- = 1.0 \text{ L} \times \frac{6.0 \text{ mol}}{\text{L}} = 6.0 \text{ mol}$$

First, we assume all the Cd^{2+} precipitates (using stoichiometry):

	Cd^{2+} +	2 OH^- →	$Cd(OH)_2$
B	0.0012		0
A		6.0	
M	–0.0012	–0.0024	+0.0012
A	0	5.9976	0.0012

New $[OH^-]$ = 5.9976 mol/101 L = 0.0594 M
Now, let's see how much re-dissolves back into solution:

	$Cd(OH_2)$ ⇆	Cd^{2+} +	2 OH^-
I	–	0	0.0594
C	–	+ *s*	+2*s*
E	–	s	0.0594 + 2*s*

$$K_{sp} = [Cd^{2+}][OH^-]^2$$

$$2.5 \times 10^{-14} = (s)(0.0594 + 2s)^2$$

$$\therefore s = [Cd^{2+}] = 7.0 \times 10^{-12} \text{ M} \quad \text{(passes assumption)}$$

c) (3 pts) What is the mass of the solid that precipitates out?

$$? \text{ g } Cd(OH)_2 = 0.0012 \text{ mol} \times \frac{146 \text{ g}}{\text{mol}} = 0.175 \text{ g}$$

(You can solve for the quantity that re-dissolves, but since the solubility is so small, when subtracted from 0.175 g, it rounds back to 0.175 g anyway!)

9. 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) (5 pts) Find the number of moles of each element in the sample.

$$?\,mol\,C = 2.020\,g\,CO_2 \times \frac{mol\;CO_2}{44.01\,g\,CO_2} \times \frac{1\,mol\,C}{1\,mol\,CO_2} = 0.04590\,mol\,C$$

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

$$?\,g\,C = 0.0459\,mol\,C \times \frac{12.011\,g\,C}{mol\,C} = 0.5513\,g\,C$$

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

$$?\,mol\,S = (1.119\,g - 0.5513\,g - 0.0771\,g) \times \frac{mol\,S}{32.066\,g\,S} = 0.0153\,mol\,S$$

C = _____ **H =** _____ **S =** _____

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

$$C_{\frac{0.04590}{0.0153}} H_{\frac{0.0765}{0.0153}} S_{\frac{0.0153}{0.0153}} = C_3H_5S$$

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?

$$?\,mol\,gas = \frac{PV}{RT} = \frac{(0.9986\,bar)(0.0400\,L)}{(0.083145\,L \bullet bar \bullet mol^{-1} \bullet K^{-1})(300.0K)} = 0.00160\,mol$$

$$\therefore ?\frac{g}{mol} = \frac{0.234\,g}{0.00160\,mol} = 146\,g/mol$$

Answer: _____

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

$$Stoichiometric\,factor = \frac{MF\,mass}{EF\,mass} = \frac{146}{73} = 2 \qquad C_6H_{10}S_2$$