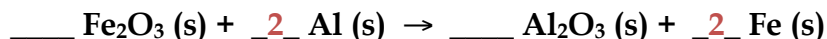


1. (20 points) Short Answer Questions.

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

Tin (II) oxide SnOSulfurous acid H₂SO₃

b) Balance the following reaction:

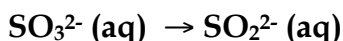


When 50.00 g of iron (III) oxide was reacted with excess aluminum, 28.65 g of solid iron was formed. The percent yield of the reaction is 81.9%.

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

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

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



OXIDATION REDUCTION # of electrons = 2

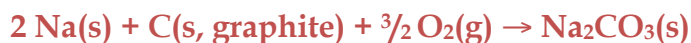
There are three ways to solve this problem:

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

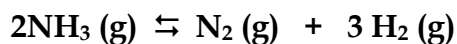
ii. Balancing the half-reaction: $2\text{H}^+ + \text{SO}_3^{2-} + 2\text{e}^- \rightarrow \text{SO}_2^{2-} + \text{H}_2\text{O}$

Since the electrons are reactants, this is a reduction

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

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

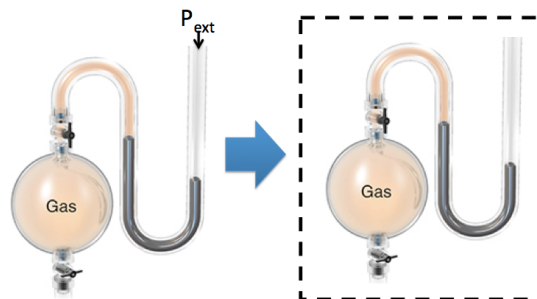
f) For the following reaction



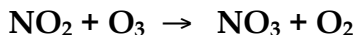
the value of K_c is 2.8×10^{-9} at 298 K. Therefore, K_p for this reaction is 1.7×10^{-6} .

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

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



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



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

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

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

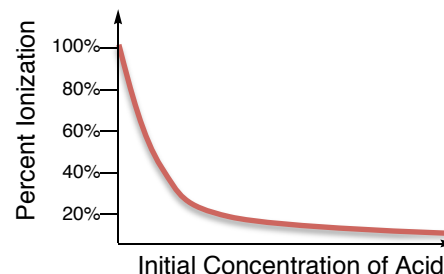
- i) Name two factors that influence the speed of a chemical reaction:

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

ii. _____

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

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



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

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

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

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

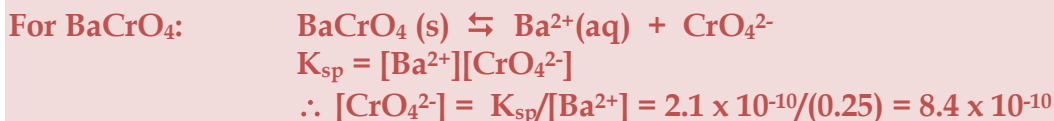
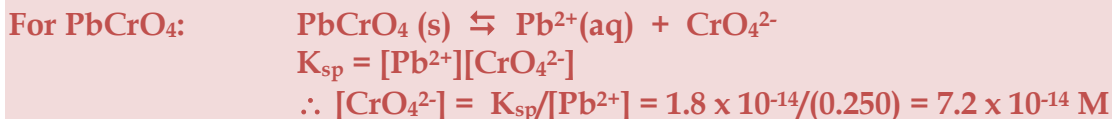
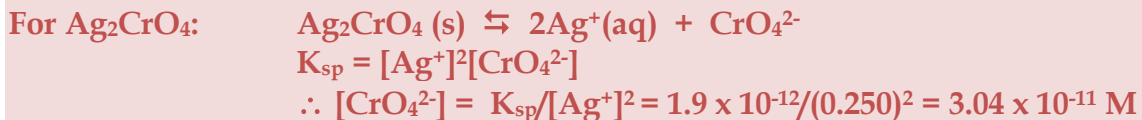
- m) The maximum number of electrons that can have the designation $3p$ is 6.

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

TRUE FALSE

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

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



First = PbCrO_4 Second = Ag_2CrO_4 Third = BaCrO_4

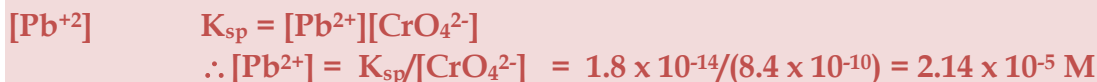
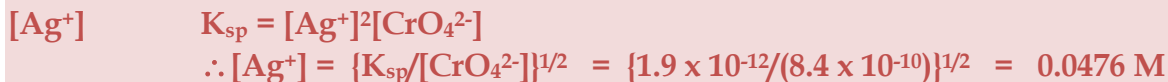
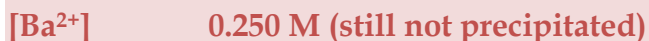
- b) (2 points) What concentration of chromate will cause the first precipitation?

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

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

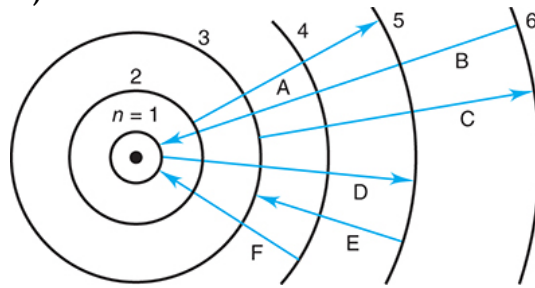
- c) (4 points) At the point *just before* BaCrO_4 begins to precipitate, what will be the concentration of all of the ions in solution?

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



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

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



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

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

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

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

Absorption A:

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

Absorption C:

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

Absorption D:

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

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

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

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

Emission B:

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

Emission E:

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

Emission F:

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

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

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

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

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

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

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

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

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

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

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

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

The OH^- comes from the ionization of ammonia:

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

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

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

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

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

Answer (circle one):

YES

NO

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

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

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

$$V = d^3$$

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

Answer: _____ **335 m** _____

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

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

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

Answer: _____ **1.06x10³⁴ atoms** _____

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

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



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

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

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

Answer: - 90.2 kJ/mol

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

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

Using the van't Hoff Equation:

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

Answer: 9.31x10⁻³

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

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

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

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

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

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

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

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

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

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

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

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

$$= 11.7 \text{ atm}$$

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

$$= 7.7 \text{ atm}$$

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

$$= 4.0 \text{ atm}$$

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

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

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

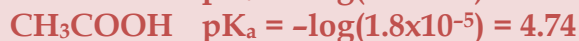
V₂ is 20% of V₁ → Therefore, P₂ is 20% of P₁

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

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

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

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



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

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

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

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

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

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

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

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

Answer: 775 mL

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

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

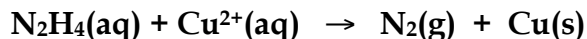
	$\text{CH}_3\text{COOH} + \text{OH}^- \rightarrow \text{CH}_3\text{COO}^- + \text{H}_2\text{O}$			
B	0.02750		0.05000	-
A		0.01544		-
M	-0.01544	-0.01544	+0.01544	-
A	0.01206	0	0.06544	-

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

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

Answer: 5.47

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



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

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

Adding the 2 half-reactions gives:



reducing agent

oxidizing agent

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

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

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

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

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

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

Answer: 0.936 L