

*Key***Chem 112000-2 Winter 2022 Final Review**

The following questions cover content from the entire quarter but in no way represent everything that you can be tested on. These questions should be supplemented with understanding of all homework problems, discussion worksheet problems, as well as the 3 midterms. Furthermore, the only additional material that should be needed to complete these questions is a calculator and a periodic table (in addition to the constants/values provided on this front page).

Some useful constants:

1. Boltzmann Constant $k = 1.38 \times 10^{-23} \text{ J/K}$
2. Avogadro Number $N_A = 6.02 \times 10^{23}$
3. Speed of light is $3 \times 10^8 \text{ m/s}$
4. Planck's constant is $6.626 \times 10^{-34} \text{ Js}$
5. Mass of electron is $9.1 \times 10^{-31} \text{ kg}$
6. 1 Joule is $6.42 \times 10^{18} \text{ eV}$
7. Gas Constant $R = 8.314 \text{ J / (mol K)} = 0.0821 \text{ (l atm) / (mol K)} = 2.00 \text{ cal / (mol K)}$
8. Specific heat capacity of ethanol: $c_{gas} = 1.702 \text{ J/g}\cdot\text{K}$ and $c_{liquid} = 2.443 \text{ J/g}\cdot\text{K}$
9. Normal boiling point of ethanol is 78.4°C
10. K_a of HCN is 4.9×10^{-9}
11. K_a of HNO_2 is 4.6×10^{-4}
12. K_b of NH_3 is 1.8×10^{-5}
13. $K_{sp} = 8.90 \times 10^{-17}$ for Ag_3PO_4

1. For the following questions, select the ONE correct answer for each multiple choice question.

(a) Which of the following is true of an unsaturated solution?

A) $Q > K_{sp}$

(B) $Q < K_{sp}$

C) $Q = K_{sp}$

D) $Q = K_{sp}^{-1}$

E) $Q = K_{sp}^2$

(b) The initial product to reactant ratio for an equilibrium reaction is found to be 2.40×10^5 . If the reaction must shift in the reverse (backwards) direction to reach equilibrium, which of the following is a possible value for the equilibrium constant, K_{eq} for this reaction?

A) -2.40×10^5

(B) 2.40×10^{-5}

C) 2.40×10^5

D) 2.40×10^{15}

E) 0

(c) The following equilibrium was established in a reaction flask



Which of the following actions would result in an increase in [X] in the reaction flask?

A) Adding more solid Y

B) Adding a catalyst

C) Increasing pressure on the flask

D) Increasing the flask's volume

(E) None of the above

- (d) What is the K_a for a 0.10 M weak acid solution that is found to be 1.50% ionized?
- A) 1.5×10^{-3}
 - B) 1.5
 - C) 0.23
 - D) 2.3×10^{-5}
 - E) 2.3×10^{-6}
- (e) Which of the following combinations of equal volumes of solution will result in a buffer?
- 1. 0.1 M HCl + 0.1 M NH₃
 - 2. 0.1 M HNO₂ + 0.05 M NaOH
 - 3. 0.05 M HNO₂ + 0.05 M NH₃
- A) 1 only
 - B) 2 only
 - C) 3 only
 - D) 1 and 3 only
 - E) 2 and 3 only
- (f) Who discovered the exact location of electrons in atoms?
- A) Rutherford
 - B) Bohr
 - C) Schrodinger
 - D) Heisenberg
 - E) None of the above
- (g) Which of the following is certainly **true** about a single, neutral atom of manganese?
- A) It has a mass of exactly 54.95 atomic mass units.
 - B) Its two highest energy electrons are located in a spherically-shaped orbital.
 - C) Its nucleus contains as many protons as it does neutrons.
 - D) To form a +1 cation, an electron will be removed from a d orbital.
 - E) It contains unpaired electrons.

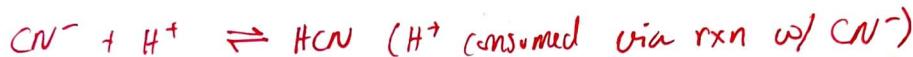
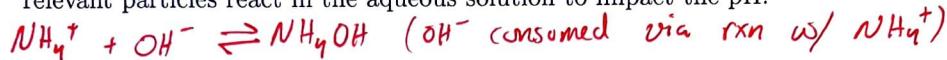
(h) Which of the following statements regarding Valence Bond Theory is **not** true?

- A) With a set of hybridized atomic orbitals, half of the orbitals are anti-bonding orbitals.
- B) Lone pairs of electrons on the central atom of a molecule are located in hybrid orbitals.
- C) There are four orbitals in a set of sp^3 hybridized orbitals.
- D) An orbital hybridization of sp^4 is impossible, even in a trigonal bipyramidal molecule.
- E) An atom of phosphorus does not need to promote any electrons before it can hybridize its orbitals to engage in bonding with hydrogen atoms to form the molecule PH_3 .

(i) Select the atom or ion with the incorrect electronic configuration:

- A) Mo: $[Kr]5s^14d^5$
- B) Cu^+ : $[Ar]4s^13d^9$
- C) Ce: $[Xe]6s^25d^14f^1$
- D) Eu^{+2} : $[Xe]4f^7$

2. Would you expect a solution of aqueous ammonium cyanide to be acidic, basic, or neutral? As part of your explanation, please include chemical equations showing how relevant particles react in the aqueous solution to impact the pH.



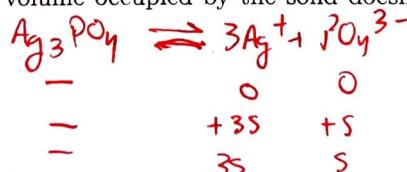
Both cause rightward shift in water equilibrium. We can see which has greater effect on pH by looking at K_a 's.

$$K_a \text{ of } \text{NH}_4^+ = \frac{1.00 \times 10^{-10}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-6}$$

$$K_b \text{ of } \text{CN}^- = \frac{1.0 \times 10^{-10}}{4.9 \times 10^{-7}} = 2.04 \times 10^{-6}$$

Since $K_b \text{ of } \text{CN}^- > K_a \text{ of } \text{NH}_4^+$, CN^- reacts more fully than NH_4^+ and forms more OH^- . So should be basic.

3. What minimum volume of pure water would be needed to dissolve exactly 1.00 g of Ag_3PO_4 ? (Assume the volume occupied by the solid doesn't contribute to the overall solution volume.)



$$K_{sp} = [\text{Ag}^+]^3 [\text{PO}_4^{3-}] = (3S)^3 S = 27S^4$$

$$\Rightarrow 8.90 \times 10^{-17} = 27S^4 \Rightarrow S = 4.26 \times 10^{-5} \text{ M Ag}_3\text{PO}_4$$

$$1.00 \text{ g Ag}_3\text{PO}_4 \times \frac{1 \text{ mol}}{418.67 \text{ g}} = 2.39 \times 10^{-3} \text{ mol Ag}_3\text{PO}_4$$

$$V = \frac{n}{M} = \frac{2.39 \times 10^{-3} \text{ mol Ag}_3\text{PO}_4}{4.26 \times 10^{-5} \text{ M}} = \boxed{56.1 \text{ L pure water}}$$

4. Imagine that a stable atom of $^{296}_{117}\text{Q}$ were discovered.

(a) Write the abbreviated (noble gas shortcut) ground state electron configuration for Q.

$$[\text{Rn}] 7s^2 6d^1 5f^{14} 6d^9 7p^5$$

or

$$[\text{Rn}] 7s^2 5f^{14} 6d^{10} 7p^5$$

(b) Which element would you expect Q to be most similar to in terms of chemical reactivity? Why?

Elements are most like those in the same group. So Q should be like At.

(c) Write a set of quantum numbers that would represent a valence electron in the highest energy orbital occupied in an element of Q.

$$n=7 \quad l=1 \quad m_l = 0, \pm 1 \quad m_s = \pm \frac{1}{2}$$

(d) Would you expect a neutral atom of Q to be paramagnetic? Why?

Q has 1 unpaired e⁻ \Rightarrow yes I expect paramagnetic

(e) To make an atom of this nuclide smaller in size, would you want to add or take away an electron? Explain.

Taking e⁻ away \Rightarrow same Z_{eff} with less e⁻. So we get a smaller radius.

5. When a glass tube full of hydrogen gas is electrified, we only see 3 specific wavelengths of light when viewing the tube through prism glasses. Respond to each of the following related questions, using 100 words or fewer for each response.

- (a) Describe the atomic level process that leads to the production of visible light in this experiment.

- When atoms absorb E, their e^- uses specific E to jump to higher E levels.
- Relaxation causes some amount of E to be released.
- Quanta/photon of E are associated with specific wavelengths of EM radiation that fall in visible region.

- (b) Why do we only see specific, distinct wavelengths of light in that experiment as opposed to the full rainbow spectrum?

There is a limited # of unique E transitions that an e^- can make. This results in only very specific amounts of E being released involved in each e^- transition.

- (c) Were those the only wavelengths of electromagnetic radiation given off during the process of giving energy to the hydrogen atoms? Explain.

Nope. Only those that fall in the visible region. e^- transitions of higher & lower E can fall in UV or IR regions.

6. Consider the following three species: O_2 , O_2^{2+} , and O_2^{2-} .

- (a) How do these three species compare in terms of bond length?

O_2^{2+} (10 valence e^-) \Rightarrow triple bond

Bond length
 $O_2^{2+} > O_2 > O_2^{2-}$

O_2 (12 valence e^-) \Rightarrow double bond

O_2^{2-} (14 valence e^-) \Rightarrow single bond

- (b) How can O_2 be magnetic even though it has an even number of total valence electrons?

When filling MO diagram of O_2 , there must be at least 1 unpaired e^- .

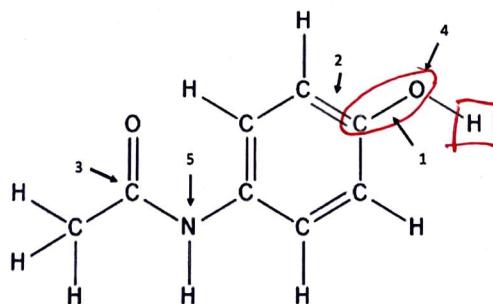
7. In terms of electron configuration, shielding, and/or effective nuclear charge, explain the overall location of the most reactive non-metals on the Periodic Table (Don't just state trends!)

- Non-metals react by gaining e^-
- Most reactive non-metals in top right of PT.
- Trend excludes Noble gases.

Across PT, e^- added to same energy level, but increasing Z_{eff} . Can pull in e^- closer. Down a group, electrons added in increasingly distant energy levels, but greater shielding \Rightarrow lower Z_{eff} .

Both of these cause reactivity to max out in upper right (at Fluorine). Easiest to add due to poor shielding: high Z_{eff} .

8. Consider the following molecule of acetaminophen (Tylenol), in which all bonds between atoms are shown but any lone pairs that exist on atoms are not shown:



$c(sp^2)$
 $O(sp^3)$

- What are the hybridization of the orbitals in C and O, respectively in bond 1? $c(sp^2)$
 $O(sp^3)$
- How many σ and π bonds, respectively, are involved in bond 2? $1\sigma, 1\pi$
- What should the geometry of the molecule be around atom 3? $Tetrahedral$
- What would you estimate the $C-O-H$ bond angle to be around atom 4? $\angle 109.5^\circ$
- What kinds of orbital does the lone pair of electrons on atom 5 occupy? sp^3
- Which carbon/oxygen bond in the molecule should be the longest? Circle it.] See above.
- Which hydrogen is the most acidic? Box it.

9. Consider the ionization of pure water: $\text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{OH}^-(\text{aq})$.

T [°C]	K_w
10	2.93×10^{-15}
25	1.00×10^{-14}
40	2.92×10^{-14}

- (a) Is the forward process endothermic or exothermic? Explain using the table of data provided.

K_w increases w/ Temp. Rxn is endothermic.

- (b) How would you expect the pH of pure water to change as the temperature increases?

Since K_w increases w/ Temp. $[\text{H}^+]$ increases w/ temp.

So pH will decrease.

- (c) Is pure water at higher temperatures acidic, basic, or neutral? Explain.

Even though pH decreases, pOH also increases.

So $[\text{H}^+] = [\text{OH}^-]$ in pure water always.

So neutral

10. 216.2 kJ of energy are given off as 235.0 grams of ethanol ($\text{CH}_3\text{CH}_2\text{OH}$) are cooled in a sealed flask from 100°C down to 60.0°C .

- (a) Given this (along with data on the front page), calculate the vapor pressure (in mm Hg) of the ethanol in the container once it reaches a temperature of 60.0°C .

$$\eta_{\text{tot}} = MC_{\text{gas}} \Delta T + n\Delta H_{\text{vap}} + mC_{\text{lig}} \Delta T$$

$$216.2 \text{ kJ} = (235.0)(1.702)(78.4 - 100) + (235)\left(\frac{1 \text{ mol}}{46.0 \text{ g}}\right)\Delta H_{\text{vap}} + (235)(2.443)(60.0 - 78.4)$$

$$\Delta H_{\text{vap}} = +38.56 \text{ kJ/mol}$$

Normal BP of EtOH $\Rightarrow 78.4^\circ\text{C}$ has vapor pressure of 760 mm Hg.

Using $\ln K_p = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right)$, we get

$$\ln\left(\frac{P_2}{760 \text{ mm Hg}}\right) = -\frac{\Delta H}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) = \left(\frac{-38.560 \text{ J/mol}}{8.314 \frac{\text{J}}{\text{mol K}}}\right)\left(\frac{1}{333 \text{ K}} - \frac{1}{351.9 \text{ K}}\right)$$

$$\Rightarrow P_2 = 366 \text{ mm Hg}$$

- (b) The vapor pressure of propane ($\text{CH}_3\text{CH}_2\text{CH}_3$) at 60.0°C is significantly higher than that of ethanol at the same temperature, even though their molar masses are quite similar. Explain why.

EtOH has H-bonding whereas propane only has dispersion forces. H-bonding stronger so more energy required to separate them, compared to propane. So at any given temperature, there should more propane in the gas phase than EtOH.

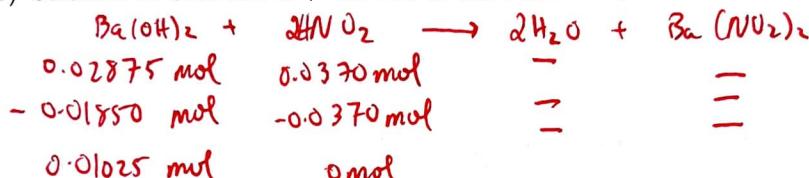
11. Determine the pH of each of the following solutions to two decimal points.

(a) Solution A: A 125 mL solution of 0.230 M $\text{Ba}(\text{OH})_2$.

$$0.230 \text{ M } \text{Ba}(\text{OH})_2 \times \frac{2 \text{ mol OH}^-}{1 \text{ mol}} = 0.460 \text{ molality OH}^-$$

$$\rho\text{OH} = -\log [\text{OH}^-] = 0.337 \quad \rho\text{H} = 14 - \rho\text{OH} = \boxed{13.66}$$

(b) Solution B: Solution A + 200 mL of 0.185 M HNO_2 .



Since $\text{Ba}(\text{OH})_2$ in excess. $0.01025 \text{ mol } \text{Ba}(\text{OH})_2 = 0.0205 \text{ mol OH}^-$

$$M = \frac{0.0205 \text{ mol}}{(0.125 + 0.200) \text{ L}} = 0.0631 \text{ M OH}^-$$

$$\rho\text{OH} = -\log (0.0631) = 1.20 \quad \rho\text{H} = 14 - \rho\text{OH} = \boxed{12.80}$$

(c) Solution C: Solution B + another 200 mL of 0.185 M HNO_2 .

$$(0.185 \text{ M})(0.400 \text{ L}) = 0.074 \text{ mol HNO}_2$$

$(0.230 \text{ M})(0.125 \text{ L}) = 0.02875 \text{ mol Ba}(\text{OH})_2$. We will have 0 $\text{Ba}(\text{OH})_2$.

and 0.0165 mol HNO_2 left over.

$$0.02875 \text{ mol } \text{Ba}(\text{OH})_2 \times \frac{1 \text{ mol } \text{Ba}(\text{NO}_2)_2}{1 \text{ mol } \text{Ba}(\text{OH})_2} \times \frac{2 \text{ mol NO}_2^-}{1 \text{ mol}} = 0.0575 \text{ mol NO}_2^- \text{ present as well.}$$

$$\rho\text{H} = -\log (4.6 \times 10^{-4}) + \log \left(\frac{0.0575 \text{ mol NO}_2^-}{0.0165 \text{ mol HNO}_2} \right)$$

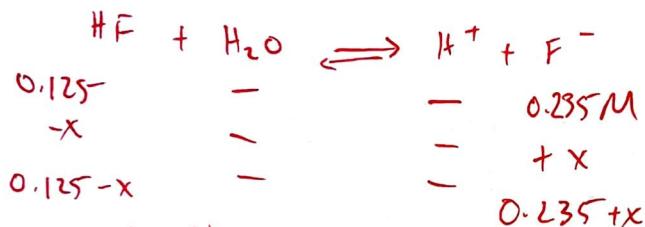
$$= 3.337 + 0.542 = \boxed{3.88}$$

12. How many grams of KOH must be added to 2.00 total L of a buffer solution made up of 0.125 M HF and 0.235 M KF in order to change its pH by 0.20 pH units? (Assume no change in total solution volume upon addition of solid.)

pH of original buffer:

$$\text{pH} = \text{pK}_a + \log \frac{\text{Base}}{\text{Acid}} = -\log(3.5 \times 10^{-4}) + \log \left(\frac{0.235 \text{ M F}^-}{0.125 \text{ M HF}} \right) = 3.73$$

Change by 0.20 units \Rightarrow target pH = 3.93. KOH reacts to give F⁻ from HF. So:



$$\text{pH} = \text{pK}_a + \log \left(\frac{\text{base}}{\text{acid}} \right) \Rightarrow 3.93 = -\log(3.5 \times 10^{-4}) + \log \left(\frac{0.235+x}{0.125-x} \right)$$

$$\Rightarrow 2.979 = \frac{(0.235+x) \text{ M F}^-}{(0.125-x) \text{ M HF}} \Rightarrow x = 0.0344 \text{ M HF react.}$$

So 0.0344 M KOH needed.

$$0.0344 \text{ M KOH} \times 2.00 \text{ L} \times \frac{56.1 \text{ g}}{\text{mol}} = \boxed{3.86 \text{ g KOH}}$$

13. (a) Using the materials provided below, describe precisely how you would make 3.0 L of a pH 10.2 buffer solution. Indicate the exact quantities (in units of L or grams) of each component that would be needed to establish your buffer system (You must use exactly 250 mL of which ever acid or base you choose.) Show all relevant calculations.

		pK_a
Acetic acid	HCH_3CO_2	$K_a = 1.8 \times 10^{-5}$
Chlorous acid	HClO_2	$K_a = 1.1 \times 10^{-2}$
Iodic acid	HIO_3	$K_a = 1.7 \times 10^{-1}$
Ammonia	NH_3	$K_b = 1.8 \times 10^{-5}$
Aniline	$\text{C}_6\text{H}_5\text{NH}_2$	$K_b = 3.9 \times 10^{-10}$
Methylamine	CH_3NH_2	$K_b = 4.4 \times 10^{-4}$

Table 1: Dissociation Constants at 25°C

Materials provided:

1. 1.5 M solutions of each acid/base in the table.
- Unlimited masses of each of the following: $\text{NaCH}_3\text{CHO}_2$ (s), NH_4Cl (s), NaClO_4 (s), $\text{CH}_3\text{NH}_3\text{Cl}$ (s), NaIO_3 (s), $\text{C}_6\text{H}_5\text{NH}_3\text{Cl}$ (s).

$$\text{pH} = pK_a + \log \frac{\text{Base}}{\text{Acid}} \Rightarrow 10.2 = 10.64 + \log \left(\frac{\text{base}}{\text{Acid}} \right) \Rightarrow \frac{\text{base}}{\text{Acid}} = 0.363$$

Choose WA/WB with pK_a closest to target pH.

$$1.5 \text{ M} \times 0.25 \text{ L} = 0.375 \text{ mol base added.} \Rightarrow \frac{0.375}{\text{Acid}} = 0.363$$

$$\Rightarrow 1.033 \text{ mol } \text{CH}_3\text{NH}_3^+ \text{ needed} \Rightarrow 69.7 \text{ g } \text{CH}_3\text{NH}_3\text{Cl} \text{ needed.}$$

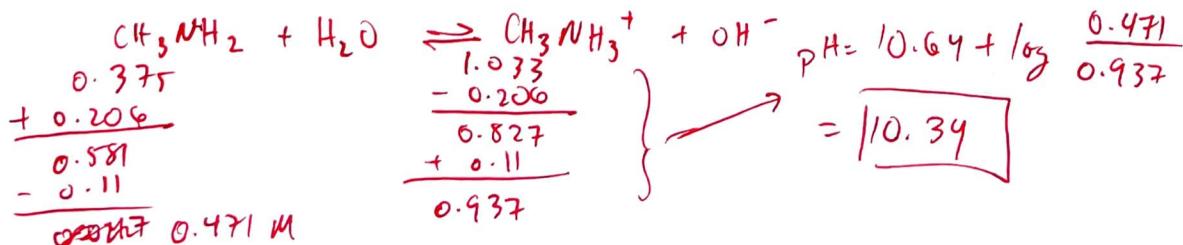
So,

$69.7 \text{ g } \text{CH}_3\text{NH}_3\text{Cl}$
$250.0 \text{ mL of } 1.5 \text{ M } \text{CH}_3\text{NH}_2$
$2.75 \text{ L } \text{H}_2\text{O}$

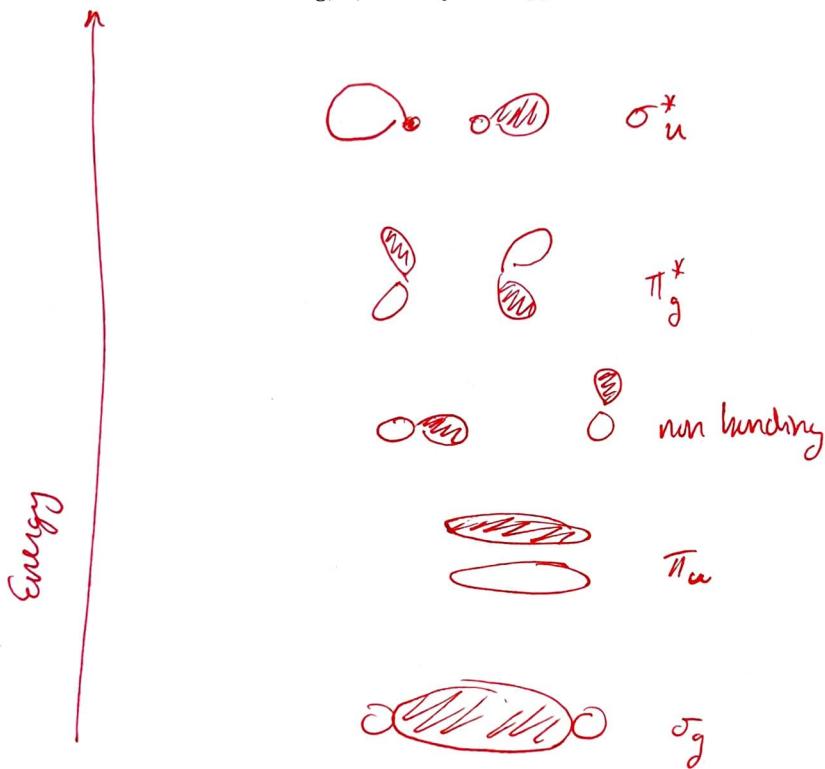
- (b) After you've made the buffer in part (a), you add in 12.5 g of $\text{Sr}(\text{OH})_2$ (s) and 50.0 mL of 2.2 M HCl. What is the final pH of the solution after everything has reacted?

$$12.5 \text{ g } \text{Sr}(\text{OH})_2 \rightarrow 0.206 \text{ mol } \text{OH}^- \text{ reacts with } \text{CH}_3\text{NH}_3^+$$

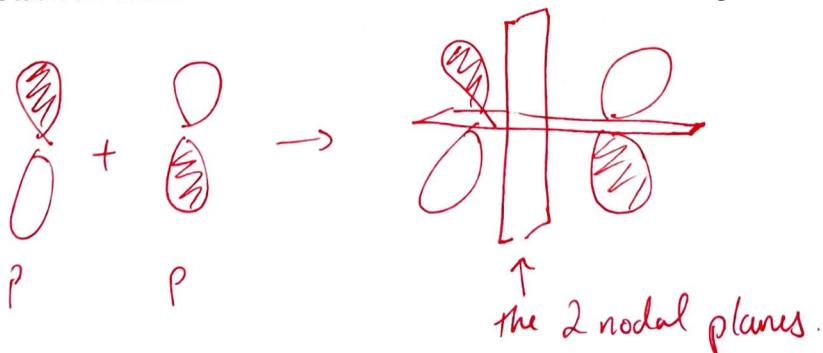
$$0.05 \text{ L} \times 2.2 \text{ M} = 0.11 \text{ mol HCl} = 0.11 \text{ mol H}^+ \text{ reacts with } \text{CH}_3\text{NH}_2$$



14. Draw a picture showing all molecular orbitals created by taking linear combination of all 2p orbitals with each other. Label them from lowest energy to highest energy and state each whether g, u, or no symbol applies.



15. Draw a picture showing a linear combination of atomic orbitals that each produce one molecular orbital containing 2 nodes. Note the nodes must involve the internuclear axis. Please label the atomic and molecular orbitals and state whether each is g or u.



16. Suppose we have both gold foil, and gaseous gold atoms.

(a) Explain the difference between ionization energy and the work function.

Ionization Energy: Energy required to remove e⁻ from gaseous atom [neutral].

Work function: Energy required to remove e⁻ from a bulk solid.

(b) Suppose we hit the gold foil with 100 nm light and observe electrons ejected moving at 1.57×10^6 m/s. What is the work function for gold in eV?

$$E = \frac{hc}{\lambda} = \frac{(6.626 \times 10^{-34} \text{ Js})(3 \times 10^8 \text{ m/s})}{10^{-7} \text{ m}} = 1.988 \times 10^{-18} \text{ J}$$

$$\frac{1}{2}mv^2 = \frac{1}{2}(9.8 \times 10^{-31} \text{ kg})(1.57 \times 10^6 \text{ m/s})^2 = 1.121 \times 10^{-18} \text{ J}$$

$$\Phi = \underbrace{(1.988 \times 10^{-18} - 1.121 \times 10^{-18}) \text{ J}}_{2 \text{ size phys}} \times \frac{6.42 \times 10^{18} \text{ eV}}{\text{Joule}}$$

$$= \boxed{5.6 \text{ eV}}$$

(c) Suppose we hit the gaseous gold atoms with 100 nm light and the slowest electrons we observe move at 1.05×10^6 m/s. What is the first ionization energy of gold in eV?

$$E = 1.988 \times 10^{-18} \text{ J} \text{ (same as above).}$$

$$\frac{1}{2}mv^2 = \frac{1}{2}(9.8 \times 10^{-31} \text{ kg})(1.05 \times 10^6 \text{ m/s})^2 = 5.016 \times 10^{-19} \text{ J}$$

~~$$\Phi \quad IE = (E - \frac{1}{2}mv^2) \frac{6.42 \times 10^{18} \text{ eV}}{\text{Joule}} = 9229 \boxed{9.5 \text{ eV}}$$~~

(d) Which electron has the greater de Broglie wavelength? Compute it.

$$\lambda_{DB} = \frac{h}{p} = \frac{h}{mv} \text{ . smaller } v \Rightarrow \text{bigger } \lambda_{DB} \text{ . So part c.}$$

$$\frac{6.626 \times 10^{-34} \text{ Js}}{(9.1 \times 10^{-31} \text{ kg})(1.05 \times 10^6 \text{ m/s})} = \boxed{6.93 \times 10^{-10} \text{ meters}}$$

- (e) Which subshell will the electron be emitted from in the gaseous gold atoms? Estimate Z_{eff} for this electron. Au is $[Xe] 4f^{14} 5d^{10} 6s^1$

$\boxed{\text{The } 6s \text{ subshell}} \quad 5d, 5p; 5s \text{ shell filled} \Rightarrow 18 e^- \text{ at } 0.85, 60 e^- \text{ in } n-2 \text{ or lower.}$

$$79 - 60 - 0.85 = \boxed{3.7 = Z_{\text{eff}}}$$

- (f) Estimate the orbital energy for the electron that is ejected during ionization.

$$E_n \sim -R_H \left(\frac{Z_{\text{eff}}}{n} \right)^2 \quad n=6$$

$$\Rightarrow -13.6 \text{ eV} \left(\frac{3.7}{6} \right)^2 = \boxed{-5.17 \text{ eV}}$$

- (g) Estimate the first ionization energy for gold using the orbital energy. How close did we get to the experimental value? If there are discrepancies, comment on them.

$$I E_\alpha = -E_\alpha \Rightarrow 5.17 \text{ eV} \text{ (theoretical).}$$

We are off. More than likely, our Hartree approximation of the orbital energy is not correct (especially since we have one f electron.) Could be improved via proper electronic structure calculations.

- (h) If you did the previous parts correctly, you will have used the Hartree approximation and Koopman's theorem. What are each's key assumption. Finally, identify which parts above you used each for.

Hartree: e^- move in an effective field generated by the nuclei and mean $e-e$ coulombic repulsion.

Used in part (f)

Koopmans: Energy of orbitals the same after losing one e^- .

part (g)