Final Exam Review

A. Uncertainty, Dilutions, and Tolerance
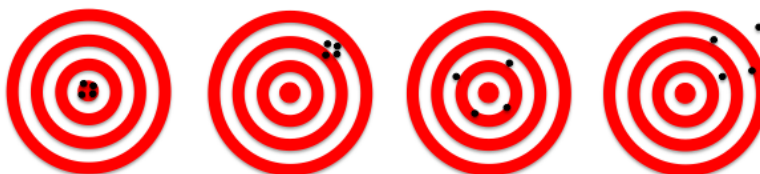
1. Define:

   (a) Error -

   (b) Mean -

   (c) Dispersion -

   (d) Range -

   (e) Standard deviation -

2. Characterize each target above as one of the following:

   (a) Accurate and Precise
   (b) Not Accurate and Not Precise
   (c) Not Accurate but Precise
   (d) Accurate but not Precise

3. Which of the above demonstrate:

   (a) Systematic error
   (b) Random error

4. *Determine* another name for systematic and random errors.

5. Sketch a picture of a target, like those above, that shows a blunder.

6. What is the difference between tolerance and percent relative tolerance?

7. How would you calculate a percent relative standard deviation (%RSD)?

8. Sketch serial and parallel dilution schemes.

9. Sketch a micropipet, Mohr pipet, and a volumetric pipet.

10. Would you rather use a volumetric pipet or a Mohr pipet? When might you want to use the other?

11. What is the difference between absolute and relative uncertainty?

12. How does the tolerance of glassware affect the precision and accuracy of a measurement?

13. What are two measures of dispersion and how are they fundamentally different?

14. What is the difference between a sample standard deviation, s, and the standard deviation of the mean $\frac{s}{\sqrt{n}}$?

15. How many significant figures are there in the following measurements?

    (a) 300.0 cm

    (b) 2.5×10^{-4} V

    (c) 0.0000006 J

    (d) 25 kcal

16. How many significant figures are there in the following products?

    (a) 300.0 cm * 25 cm

    (b) 8.31451 J/mol/K * 350 K

    (c) 0.0000006 J + 3 J

17. For the list of numbers [3, 5, 9, 9, 0, 9, 4, 8, 5, 1], calculate the

    (a) Mean

    (b) Range

    (c) Standard deviation

    (d) Standard deviation of the mean

18. For each of the following predict the effect on the mean and dispersion.

    (a) Knocking over a beaker and spilling half of the solution

    (b) Using an incorrectly calibrated balance

    (c) Taking turns with your lab partners for collecting measurements

19. Classify the errors above as either random, systematic or blunders.

20. If the mean of the list above was expected to be 7.5, how would you characterize the data with respect to accuracy? Precision?

21. If the student recording these measurements recorded a 9 instead of a 6 what could be done to the data?

22. Complete the table below.

Capacity (mL)	Tolerance (+/- mL)	%Relative Tolerance
10	0.02	
25	0.03	
50	0.05	
100	0.08	
200	0.10	
250	0.12	
500	0.20	
1000	0.30	
2000	0.50	

23. Which of these would you prefer to use?

24. If you were to make 50 mL of a solution which would you prefer?

B. Instrumental Calibration, Spectroscopy, and Beer's Law

1. Using the calibration curve below, identify the analyte, linear regression line, and the correlation coefficient.
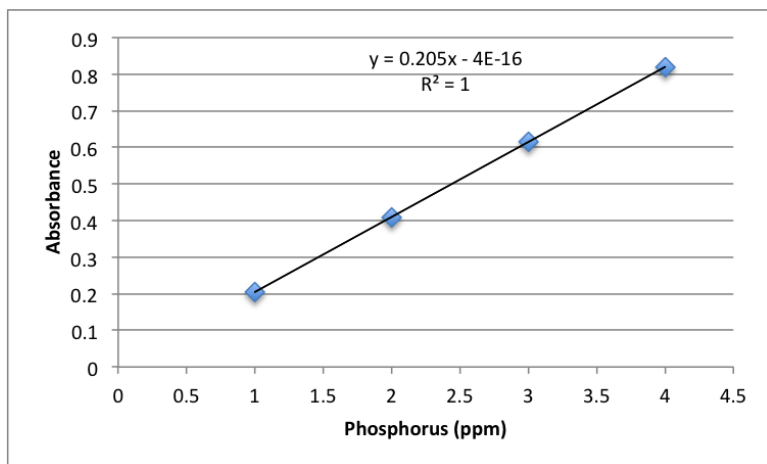
2. More points could have been left on the graph above, giving the graph below. Should these points be included? What is the linear dynamic range of this analysis method?
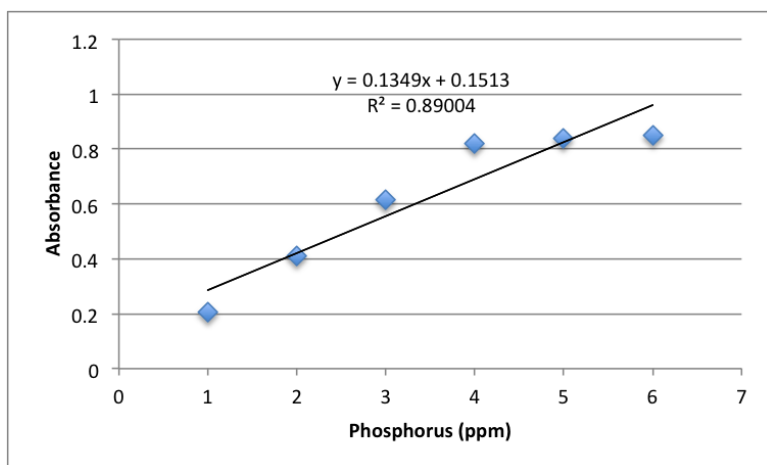
3. An analyst tested 7 blanks to assess the minimum detectable signal (MDS) for her experimental method. If the signals of these blanks were 0.003, 0.007, 0.004, 0.006, 0.008, 0.004, and 0.005, what is the minimum detectable signal?

4. If the corresponding calibration curve had an equation of $y = 0.0077x + 0.0063$, what is the lower limit of detection for her method?

5. If the standard deviation of the low concentration standards were 0.0024, approximate the LLOQ for the method. Also approximate the LLOD and compare it to your exact measurement.

6. If the signal of this curve were absorbance, and path length were 1 cm, what would the molar absorptivity constant be? The units of concentration are ppb.

7. Calculate the transmittance corresponding to 0 ppb concentration using the information above.

8. Define:

    (a) Wavelength -

    (b) Frequency -

    (c) Photon -

    (d) Absorption -

    (e) Spectrum -

    (f) Transmittance -

    (g) Absorbance -

9. What is the relationship between wavelength, frequency and the speed of light, c? What about the relationship between energy, Planck's constant, h, and these other factors?

10. How many legs are there in a mole of spiders?

11. What is the mathematical relationship between transmittance and absorbance?

12. Calculate the wavelength of light needed for an atomic absorbance process requiring 405 kJ/mol of energy. What type of light is this?

13. What does the correlation coefficient of a calibration curve say about its fit?

14. What wavelengths are associated with the following transitions?

    (a) Bonds breaking
    (b) Electronic transitions
    (c) Vibration
    (d) Rotation

15. What characteristics make molecules susceptible to each of the above transitions?

16. Identify the type of light the following molecules are most likely to interact with and how they will interact.

    (a) N_2
    (b) CO_2
    (c) H_2O
    (d) O_3

17. What is molar absorptivity? What symbols are used to represent it and what are its units?

18. What are the other factors in the Beer-Lambert law and how do they affect absorbance?

19. What is the difference between an absorption spectrum and a calibration curve? Draw an example of each.

20. What is the major difference between atomic and molecular absorption spectra?

C. Quality Assurance and Standard Additions

1. Define:

    (a) Recovery -

    (b) Spike -

    (c) Relative deviation -

    (d) Instrument performance check (IPC) -

    (e) Laboratory fortified sample matrix (LFsM) -

    (f) Spike recovery -

2. What does "sensitivity" refer to with respect to a calibration curve?

3. How would you create a reagent blank for a calibration curve?

4. What is the point of an IPC? LFSM?

5. Write down the formulae for

   (a) Spike recovery

    (b) IPC recovery

(c) Percent relative deviation

6. Using the table below and the formulae above, calculate the spike recovery, IPC recovery, and % relative deviation of the replicate samples.

Run Number	Ag (ppb)	Absorbance
1	Calibration Standards	0.000
2	2.00	0.013
3	10.0	0.076
4	20.0	0.162
5	30.0	0.245
6	50.0	0.405
7	75.0	0.598
8	100.0	0.748
9	IPC (30.0 ppb)	0.243
10	Calibration Blank	0.004
11	Sample	0.030
12	Duplicate Sample	0.032
13	LFSM (10 ppb added)	0.109
14	IPC (30.0 ppb)	0.232
15	Calibration Blank	0.003

7. Based on these calculations is the sample analysis of acceptable quality? How do you know?

8. What is the difference between the method of standard additions and a normal calibration curve? When would you want to use one over the other?

9. Describe the preparation of samples for standard additions.

10. Using the standard additions curve below calculate the concentration of the unknown assuming

(a) The graph is absorbance vs added concentration in M.

(b) The graph is absorbance vs added spike voluem in mL, 10 mL of unknown and a spike concentration of 0.10 M.

$y = 0.103x + 2.874$

Response signal, R
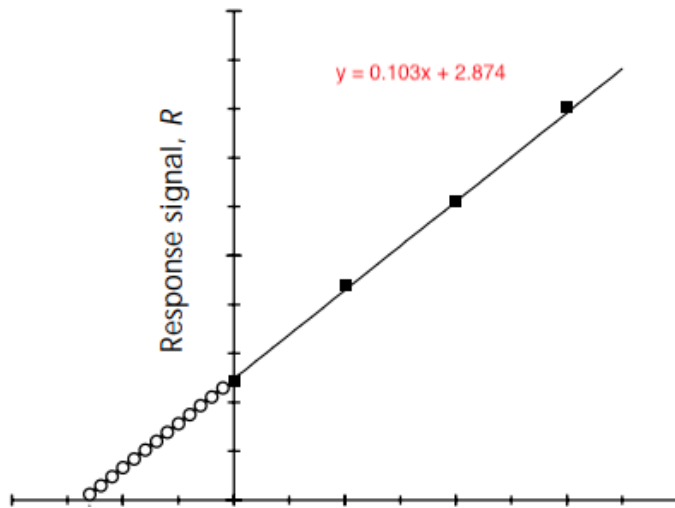
D. Rate Laws

1. The rates of chemical reactions depend on _____ factors, and they are:

2. Write an expression using Δ notation for the change in concentration of a product with respect to time.

3. Write an expression using Δ notation for the change in concentration of a reactant with respect to time.

4. For the reaction $2\,A + B \longrightarrow 3\,C + 4\,D$, express the rate of reaction in terms of:

    (a) A
    (b) B
    (c) C
    (d) D

5. Write a general rate law for equation reactants A and B with orders x and y.

6. What is the overall order for the reaction above?

7. What is the difference between an average rate and instantaneous rate? Sketch each one on a graph. Which of these do you think best describes an initial rate?

8. Identify and explain each of the terms in the equation rate $= k[A]^x[B]^y$.

9. Given an overall reaction order of 3, what are the units of the rate constant, k?

10. Using the data below determine the rate law for the reaction
$BrO_3^- + 5\,Br^- + 6\,H^+ \longrightarrow 3\,Br_2 + 3\,H_2O$.
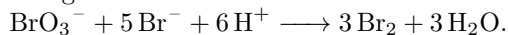
Experiment	$(BrO_3^-)_0$ [M]	$(Br^-)_0$ [M]	$(H^+)_0$	Initial Rate [M/s]
1	0.10	0.10	0.10	8.0×10^{-4}
2	0.20	0.10	0.10	1.6×10^{-3}
3	0.20	0.20	0.10	3.2×10^{-3}
4	0.10	0.10	0.20	3.2×10^{-3}

11. Based on the rate law derived above, what would be the rate of reaction if the concentration of all reactants were 0.50 M?

12. Write the general integrated rate law expression for the following reaction orders and determine what to plot versus time to get a linear graph for each one.

    (a) Zero order
    (b) First order
    (c) Second order

13. Assuming the plot of the natural logarithm of concentration vs time gave a linear curve for the first reactant, use the following table to determine the overall order of reaction.

Experiment	Reactant 1 (M)	Reactant 2 (M)	Initial Rate (M/s)
1	0.10	0.10	1.80×10^{-4}
2	0.10	0.15	4.05×10^{-4}

13

14. If it takes 1.7×10^2 s for 80% of a sample of C_4H_8 to decompose, what is the rate constant assuming first-order kinetics.

15. If the decay of Iodine-131 to Xenon-131 is first-order with a rate constant of $0.138 \ \text{d}^{-1}$, calculate the concentration of an iodine-131 solution that was initially 0.500 M after 16.7 days.

E. Equilibrium

1. Write the mass action expression corresponding to the equation $X + Y \longrightarrow 2\,Z$.

2. Define LeChatelier's principle.

3. Reaction equilibrium is _____ at the macroscopic scale but _____ at the microscopic scale.

4. What is the difference between the equilibrium constant, K, and the reaction quotient, Q?

5. When does K = Q?

6. For the following values of K, state the relationship between the equilibrium concentrations of the products and reactants.

    (a) K >> 1, [Reactant] _____ [Product]

    (b) K << 1, [Reactant] _____ [Product]

    (c) K ≈ 1, [Reactant] _____ [Product]

7. Why can consecutive equilibrium steps be simplified to a single equilibrium expression?

8. For the following, determine which way the reaction will proceed.

    (a) K > Q

    (b) K < Q

    (c) K = Q

9. Determine the *mass action expression* for the reaction $N_2 + 3\,H_2 \longrightarrow 2\,NH_3$ and determine whether there are more products or reactants if the equilibrium concentrations are $[N_2] = 1.00$ M, $[H_2] = 10.0$ M, $[NH_3] = 2.08$ M.

10. If Q for the reaction above were 5×10^{-4}, which direction would you expect the reaction to proceed?

11. Nitrogen gas (N_2), combines with oxygen gas (O_2), to form an intermediate nitric oxide (NO). NO can then react with more oxygen gas to form nitrogen dioxide (NO_2). Write the balanced equations for these reactions and show how the equilibrium expressions can be reduced to a single expression.

12. What is the equilibrium constant expression for the reverse of the previous reaction?

13. What about for the same reaction but with double all reactants and products?

F. Acid/Base

1. Using the Brønsted-Lowry conception, define:

   (a) Acid -

   (b) Base -

2. Given the acid HA, what is the conjugate base? What is the conjugate acid of HA?

3. The conjugate base of a strong acid is _____.

4. What is an "amphoteric" substance? Provide an example.

5. What values would you use to differentiate a strong acid from a weak acid?

6. What is a hydronium ion? Write its chemical formula and draw its Lewis structure. Based on the Brønsted-Lowry conception, is it an acid or a base?

7. Write the *ion product constant* for water.

8. As the strength of an acid increases, the strenght of its conjugate base _____.

9. Write the acid-dissociation constant for the hypothetical acid HA.

10. Write the base-dissociation constant for the hypotehtical base B.

11. Show how the two above expressions are related to your answer to 7.

G. pH and Ionization

1. Define:

    (a) pH $=$

    (b) pOH $=$

    (c) pX $=$

2. Write an equation for the addition of the acid HA to water.

3. Write an equation for the addition of the base B to water.

4. Write the equation for percent ionization.

5. How does the pH scale relate to the ion product constant for water?

6. How does the pK_a relate to the equilibrium concentrations of an acid and its conjugate base?

7. How does the pK_b relate to the equilibrium concentrations of a base and its conjugate acid?

8. Complete the following table:

pH	pOH	$[H^+]$	$[OH^-]$
1			
		4.7×10^{-4}	
	4		
			6.8×10^{-11}

9. Calculate the pH of a 0.250 M solution of HCl.

10. Calculate the pH of a 0.440 M solution of NaOH.

11. Using logartithm rules, derive the Henderson-Hasselbalch equation from the general K_a expression.

12. Calculate the pH of a 1.25 M solution of arsenious acid. $K_a = 6 \times 10^{-10}$

H. Distribution Plots and Polyprotic Systems

1. Sketch a distribution plot for H_2CO_3 and identify the principal species at pH $= 5$, pH $= 8$, and pH $= 11$. $K_{a1} = 4.3 \times 10^{-7}$, $K_{a2} = 5.6 \times 10^{-11}$.

2. What is the *intermediate form* for the plot above?

3. What characteristics make a good colorimetric indicator? It may be useful to write an equation showing an indicator, HInd, reacting with a base.

4. For the plot below, identify the species corresponding to each curve. Approximate the pK_as, and use the equilibrium constants sheet to identify the corresponding acid with the general formula HA_3.
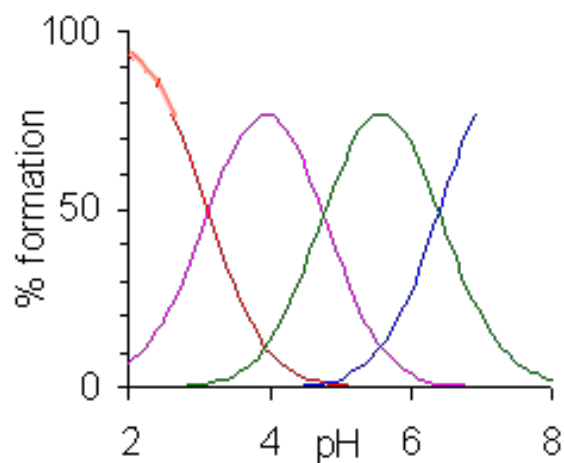
I. Conjugate Strength and Salt Solutions

1. Define the relationship between K_a and K_b for a conjugate pair.

2. Show a *hydrolysis* reaction using both the acid HA and the base B.

3. Determine whether the pH of the following salt solutions will be acidic or basic:

   (a) NH_4CH_3COO (ammonium acetate)

   (b) NH_4CN (ammonium cyanide)

   (c) $NH_4HC_2O_4$ (ammonium oxalate)

   (d) $NaCl$ (sodium chloride)

   (e) $KOCl$ (potassium hypochlorite)

4. Given $K_a = 4.7 \times 10^{-6}$ for HA, calculate K_b for its conjugate and identify its formula.

5. Calculate the pH of a 0.30 M solution of potassium hypochlorite.

J. Buffers

1. What do you look for when identifying a buffer solution?

2. Derive the buffer equation starting from an equilibrium constant expression.

3. Explain how a buffer mitigates changes in pH using reactions of a mixture of the weak acid HA and its conjugate base, A^-.

4. Where is the pH equal to the pK_a on:

    (a) An acid-base distribution plot
    (b) A titration curve

5. Which of the following solutions are buffers?

    (a) 0.100 M NH_4^+ and 0.050 M NH_3
    (b) 0.600 M CH_3COO^- and 0.050 M CH_3COOH
    (c) 0.100 M HBr and 0.100 M KBr

6. Calculate the pH corresponding to each of the solutions above.

7. Determine which of the following would be best to create a buffer with pH = 8.5, and calculate the ratio of acid:base required to make the buffer.

    (a) NH_3 and NH_4^+
    (b) HCN and CN^-
    (c) HN_3 and N_3^-

K. Titrations

1. Differentiate between the "equivalence point" and the "end point" of a titration.

2. Given an indicator that changes color at a pH of 6.5, would it be a useful indicator in the titration of 20 mL of 0.1 M acetic acid with 0.1 M NaOH? Why or why not?

3. Draw on the same axes the titration curve for the titration of:

   (a) A strong acid with a strong base
   (b) A weak acid with a strong base
   (c) A weak base with a strong acid

4. Plot the titration curve corresponding to the titration of 25 mL of 0.50 M arsenic acid with 0.50 M NaOH by calculating:

   (a) The initial pH

   (b) The pH at all half-equivalence points

   (c) The pH at all equivalence points

   (d) The pH after the addition of 5 mL of NaOH after each equivalence point

(e) The pH after the final equivalence point is exceeded by 50 mL of NaOH

5. Identify the buffer regions on the plot above.

L. Redox and Electrochemistry

1. Define:

    (a) Oxidation -

    (b) Reduction -

    (c) Anode -

    (d) Cathode -

    (e) Oxidizing agent -

    (f) Reducing agent -

2. Sketch a galvanic cell and label the anode, cathode, site of reduction, site of oxidation, salt bridge, switch, voltmeter, flow of electrons, and flow of anions through the salt bridge.

3. Given the cell diagram $\text{Zn(s)}|\text{Zn}^{2+}\text{(aq)}||\text{Cu}^{2+}\text{(aq)}|\text{Cu(s)}$, identify the cathode, anode, and which species is being reduced and which is being oxidized.

4. What defines standard electrochemical conditions?

5. What does SHE stand for in electrochemistry? What is her significance?

6. Write down the Nernst equation. Define all of its terms.

7. Write the overall cell equation for the galvanic cell composed of tin and iodine, identify which will serve as the cathode and the anode, and calculate the standard cell potential.

8. For the equation above, calculate the equilibrium constant at 298K.

9. Using the Nernst equation, calculate the cell voltage for the above reaction when the concentration of tin is 0.32 M and the concentration of iodine is 2.4 M.

10. Is the cathode the same as it was at standard conditions? If not, how can you tell?

M. Chromatography and Band Broadening

1. Define:

    (a) Stationary phase -

    (b) Mobile phase -

2. What do you know about the composition of each phase above for

    (a) Normal phase chromatography -

    (b) Reverse phase chromatography -

3. What characteristics define a good separation for a chromatography experiment?

4. What is the minimum resolution required for two peaks to be baseline resolved?

5. What factors affect the width of a peak on a chromatogram? Write an equation relating the effects of these factors to the flow rate and the breadth of the band.

6. Identify the terms associated with the symbols k', R_s, and D for chromatographic separations. Explain the importance of these terms.

7. How is the resolution of a chromatogram calculated?

8. How do the relative polarities of the stationary and mobile phase affect the retention time for a solute?

9. What effect do the following have on bandwidth?

    (a) Multiple paths

    (b) Diffusion

    (c) Mass transfer

10. Where do the three terms in the van Deemter equation come from? What do they represent?

11. On a single set of axes, sketch the relationship between band broadening and flow rate for each of the factors in the van Deemter equation and the van Deemter equation itself.
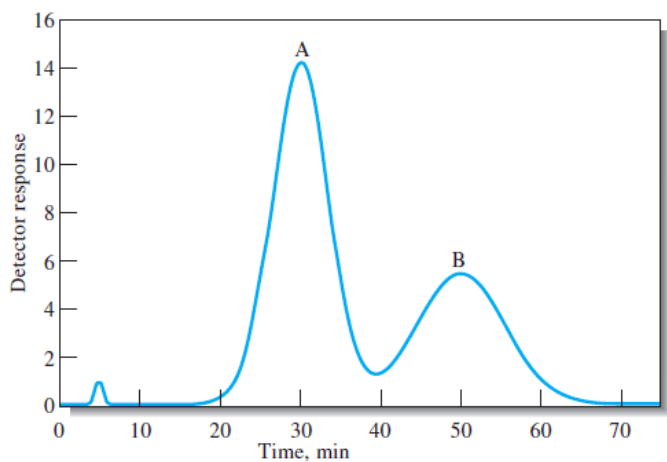
12. For the packed liquid chromatogram shown above:

(a) How long did each component spend in the stationary phase?

(b) Find the retention time for each component.

(c) Determine the retention factor for each component.

(d) What is the resolution for the two peaks?

13. Assuming A is isopropanol and B is hexane, is this an example of normal or reverse phase chromatography?

14. If the other phase were used how would this affect the elution order?

15. If B were instead propylene glycol, how would this effect the elution order?

16. For the van Deemter plot below, identify the optimum linear flow rate and the relative contributions of the factors in the van Deemter equation.