Name________________________________

Exam Two

Truth emerges more readily from error than from confusion.

Francis Bacon

You have 2.5 hours to complete this exam, which consists of three parts. Part I consists of three short answer questions and Part II has three short calculations; together, these should take you about an hour. Part III consists of a two more involved problems. Leave yourself an hour for these problems. Good Luck!

Part 1 _____/21

Part 2 _____/21

Part 3 _____/58

Total ___________

Potentially Useful Information

$S_{meas} = k_A C_A + S_{reag}$ $\qquad$ $S = k_A C_A + k_I C_I$

$K_{A,I} = k_I/k_A$ $\qquad$ $R_A = C_A/(C_A)_o$

$S_{I,A} = R_I/R_A$ $\qquad$ $E = (R_A - 1) + \{K_{A,I}(C_I)_o/(C_A)_o\}R_I$

$$(Q_{aq})_n = \{V_{aq}/(DV_{org} + V_{aq})\}^n$$

Part I – Short Answer Questions (21 points)

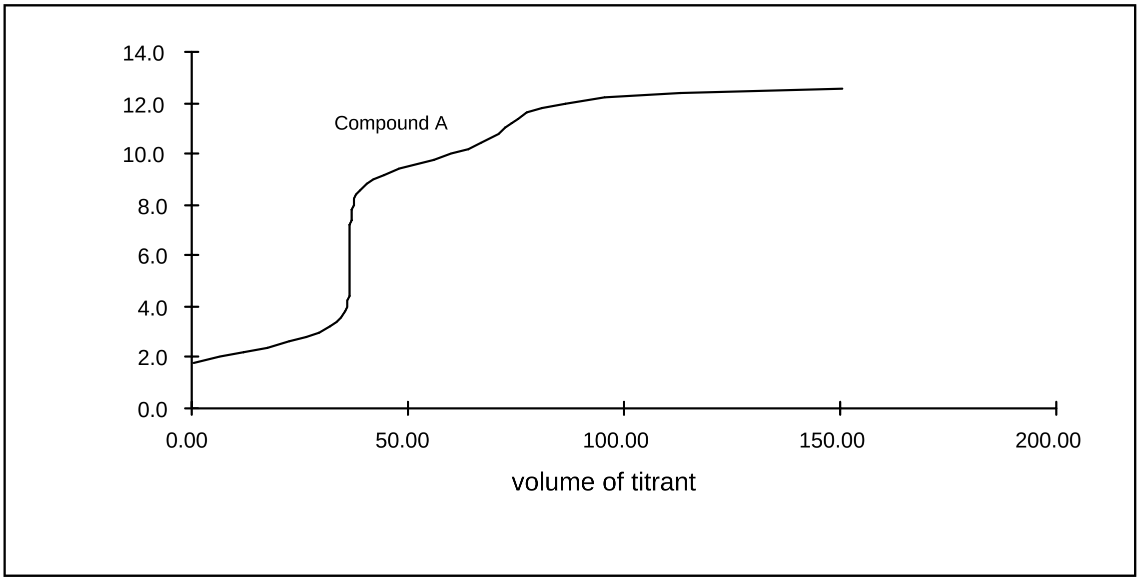
For each of the following, please provide a brief written response *using complete sentences*, being sure to address each question's main point. You may find it useful to include chemical reactions and/or sketched titration curves to illustrate your answers; however, they are just that – illustrations, not answers. A clearly explained written response, therefore, is a necessity.

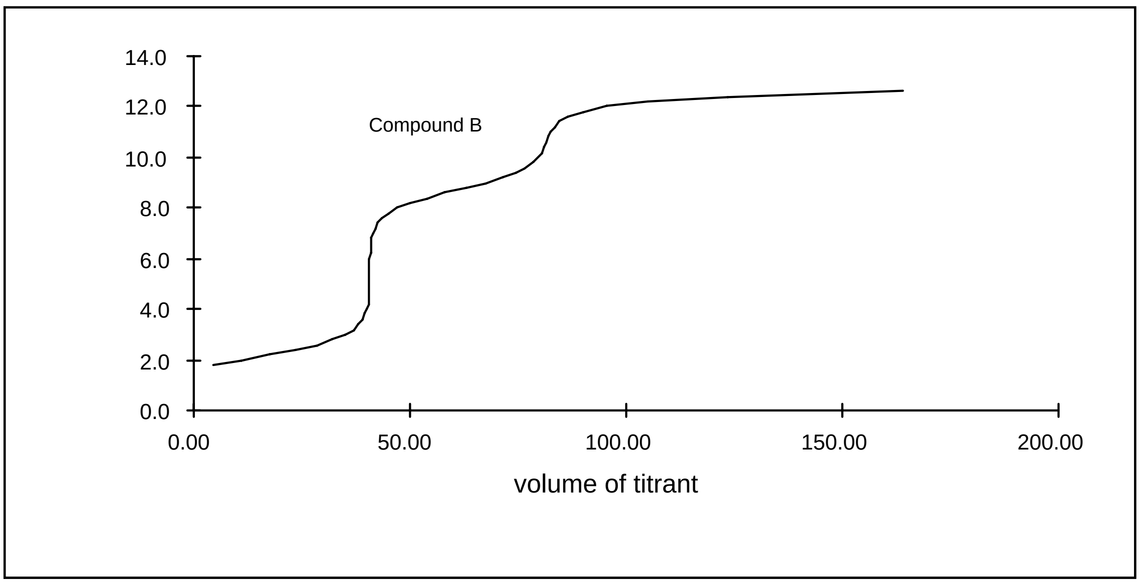
1. Liquid-liquid extractions are characterized by a partition coefficient, K_D, and a distribution ratio, D. Clearly explain the difference between these two terms, using an appropriate example to illustrate your answer.

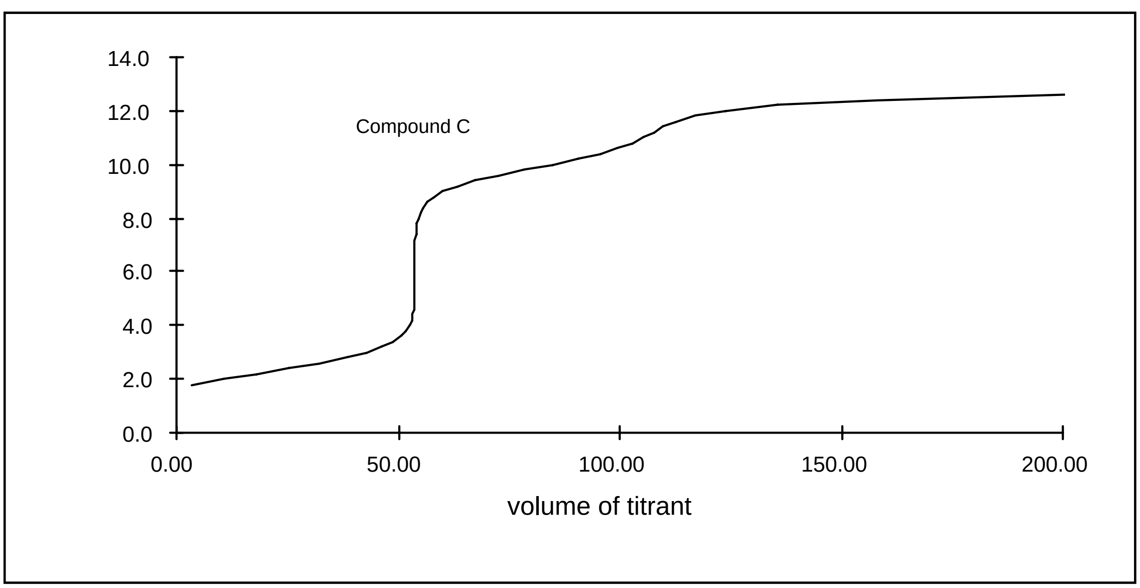
2. It is the day before your biochemistry project is due. You have three samples that you have carefully isolated and purified; they are:

amino acid	molar mass (g/mol)	pK_{a1}	pK_{a2}
isoleucine•HCl	132.2	2.32	9.75
asparagine•HCl	119.1	2.14	8.72
alanine•HCl	90.10	2.35	9.87

Unfortunately, you forgot to label your vials! Fortunately, you remember everything from Chem 352 and know that you can identify the amino acids by titrating each with NaOH. Using an automatic titrator, you obtain the three titration curves shown on the following page. Each titration is for a 0.500-g sample using 0.1032 M NaOH as the titrant. Identify the sample that is alanine•HCl. Be sure that you clearly explain how you arrived at your decision. Note that the terminology •HCl means that the amino acids are in their most acidic form, H_2A^+.


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Compound A
0.00
50.00
100.00
150.00
200.00
volume of titrant


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Compound B
0.00
50.00
100.00
150.00
200.00
volume of titrant


14.0
12.0
10.0
8.0
6.0
4.0
2.0
0.0
Compound C
0.00
50.00
100.00
150.00
200.00
volume of titrant

3. The titrimetric analysis of amino acids is complicated by the high pK_a of the $–NH_4^+$ functional group, which produces a titration break insufficient for a visual indicator. One way to overcome this problem is to use a back-titration. Briefly explain how a back-titration is carried out (identifying the solutions used) and why it produces a better end point.

Part II – Shorter Problems (21 points)

For each of the following, please carry out the requested calculation. Be sure to clearly indicate your final answer, and to mark through material you do not wish me to evaluate. Be sure, as well, to include units and to pay attention to significant figures. Partial credit is assigned, but only when there is sufficient work for evaluation.

1. In a recent paper in *Analytical Chimica Acta* [**2001**, *444*, 279-286], Vílchez and co-workers describe a spectrofluorometric method for the quantitative analysis of the antibiotic norfloxcin. In the paper, the authors note that the presence of 330 ng/mL Cu^{2+} in the presence of 2.0 ng/mL norfloxcin produces an error of +5%. What is the selectivity coefficient for the analysis of norfloxcin in the presence of Cu^{2+}?

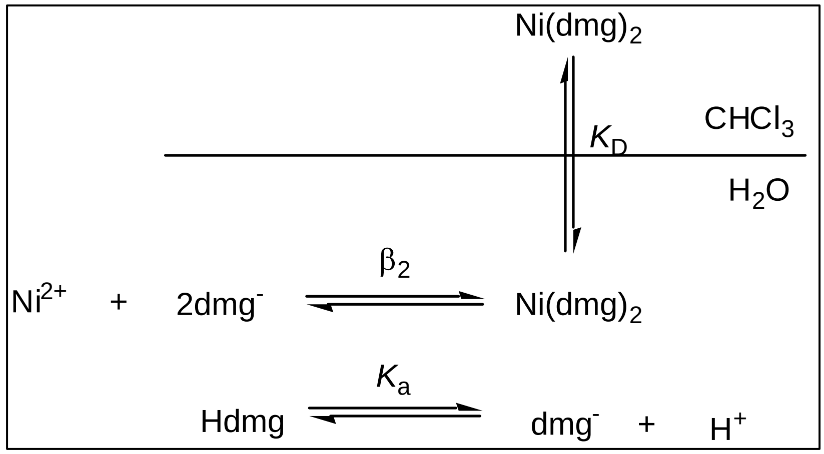
2. Knowing a solute's distribution ratio, we can design a liquid-liquid extraction that meets our analytical needs. But, how do we obtain a value for the distribution ratio? Typically, we determine the distribution ratio experimentally by taking an aqueous solution containing a known concentration of analyte, carrying out the extraction, and determining the analyte's concentration in either the aqueous phase or the organic phase. In 1911, Mylius and Hüttner determined distribution ratios for the extraction of As^{3+} into ether as $AsCl_3$. When 100.0 mL of 55.16 mM $AsCl_3$ in 6 M HCl was extracted with 50.0 mL of ether, they found that the concentration of $AsCl_3$ remaining in the aqueous phase was 17.65 mM. What is the distribution ratio under these conditions?

3. Your company recently received a shipment of salicylic acid ($C_7H_6O_3$, pK_a values of 2.97 and 13.80) to be used in the production of acetylsalicylic acid (aspirin). The shipment can be accepted only if the salicylic acid is more than 99% pure. To evaluate its purity, a 0.4208-g sample is dissolved in water and titrated to the phenolphthalein endpoint, requiring 21.92 mL of 0.1354 M KOH. Report the purity of the salicylic acid (as % w/w).

Part III – Longer Problem (58 points)

The instructions for this section are the same as those for Part II!

1. Christopherson and Sandell investigated the liquid–liquid extraction of Ni^{2+} between water and chloroform, using dimethylgloxime (dmg) as a complexing ligand. The relevant equilibria are shown to the right where K_D is 410, β_2 is 2.3 x 10^{17}, and K_a is 2.6 x 10^{-11}. Working neatly (you might find it useful to do your initial work on scratch paper and copy your final derivation to this page), show that the following relationship is correct



$$D = \frac{K_D \beta_2 K_a^2 [\text{Hdmg}]^2}{[\text{H}^+]^2 + \beta_2 K_a^2 [\text{Hdmg}]^2}$$

Be sure to show sufficient detail that your mathematical reasoning is very clear. Hint: you **must** start with an equation for *D*.

The goal of the extraction is to recover the Ni^{2+} from its aqueous matrix. Calculate the extraction efficiency for $Ni(dmg)_2$ when a 50.0 mL aqueous sample containing Ni^{2+} saturated with Hdmg, giving an equilibrium concentration for Hdmg of 5.4 mM, and at a pH of 3.5, is extracted with 25.0 mL of chloroform.

How many such extractions are needed if you wish to recover 99.9% of the Ni^{2+} in the organic phase?

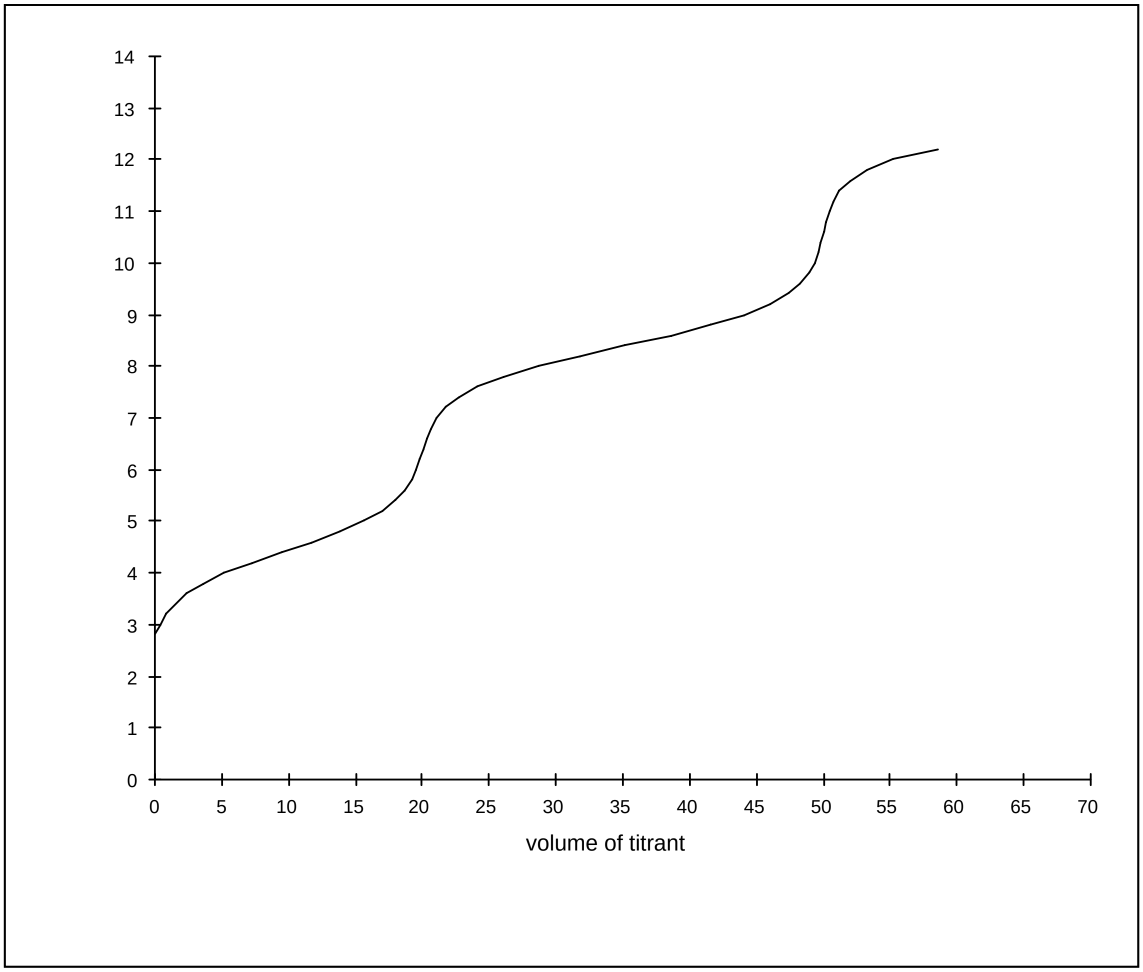
Instead of doing more extractions, it may be possible to adjust conditions such that the recovery of Ni^{2+} may be completed with a single extraction. Will increasing the pH of the aqueous phase improve extraction efficiency? Briefly justify your answer.

In addition to pH, identify at least one other way you could increase the recovery of Ni^{2+} in a single extraction. Briefly justify your choice with an appropriate explanation or calculation.

2. Shown below is the titration curve for a mixture of two monoprotic weak acids:

2–methylanilinium chloride ($C_7H_{10}NCl$, pK_a of 4.45)

3–nitrophenol ($C_6H_5NO_3$, pK_b of 8.39).



Briefly explain how you can tell that this is the titration curve for a mixture of two weak acids and not the titration curve for a hypothetical diprotic weak acid, H_2A, with pK_a values of 4.45 and 8.39.

Which of the two weak acids is responsible for the first equivalence point? Briefly justify your choice.

Suggest a suitable acid–base indicator for the first equivalence point.

The titration curve on the previous page was obtained by titrating a 2.006-g sample, dissolved in approximately 50 mL of water, with 0.200 M NaOH. What is the % w/w 3-nitrophenol in the sample?

Suppose that the 2.006-g sample had been dissolved in approximately 100 mL of water, instead of in 50 mL of water. How would this have affected the titration curve? Illustrate your answer by superimposing a sketch of the new titration curve on the original titration curve.

Table 9.4. Properties of Selected Indicators,
Mixed Indicators and Screened Indicators for Acid/Base Titrations.

Indicator	Acid Color	Base Color	pH Range	pK_a
Cresol Red	Red	Yellow	0.2-1.8	-
Thymol Blue	Red	Yellow	1.2-2.8	1.7
Bromophenol Blue	Yellow	Blue	3.0-4.6	4.1
Methyl Orange	Red	Orange	3.1-4.4	3.7
Congo Red	Blue	Red	3.0-5.0	-
Bromocresol Green	Yellow	Blue	3.8-5.4	4.7
Methyl Red	Red	Yellow	4.2-6.3	5.0
Bromocresol Purple	Yellow	Purple	5.2-6.8	6.1
Litmus	Red	Blue	5.0-8.0	-
Bromothymol Blue	Yellow	Blue	6.0-7.6	7.1
Phenol Red	Yellow	Red	6.8-8.4	7.8
Cresol Red	Yellow	Red	7.2-8.8	8.2
Thymol Blue	Yellow	Blue	8.0-9.6	8.9
Phenolphthalein	Colorless	Red	8.3-10.0	9.6
Alizarin Yellow R	Yellow	Orange/Red	10.1-12.0	-

Mixed Indicator	Acid Color	Base Color	pH Range
Bromocresol Green and Methyl Orange	Orange	Blue-green	3.5-4.3
Bromocresol Green and Chlorophenol Red	Yellow-Green	Blue-Violet	5.4-6.2
Bromothymol Blue and Phenol Red	Yellow	Violet	7.2-7.6

Screened Indicator	Acid Color	Base Color	pH Range
Dimethyl Yellow and Methylene Blue	Blue-Violet	Green	3.2-3.4
Methyl Red and Methylene Blue	Red-Violet	Green	5.2-5.6
Neutral Red and Methylene Blue	Violet-Blue	Green	6.8-7.3