

Name _____

Exam Two

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

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

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

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

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

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.

The partition coefficient, K_D , is a true equilibrium constant for the equilibrium partitioning of a specific chemical form of a compound between two phases. The distribution ratio, D , gives the equilibrium partitioning of the compound between the two phases without regard to the compound's specific chemical form, including forms that are not extracted. For example, if the compound is a weak acid, HA, and the form HA is the only one to be extracted, then

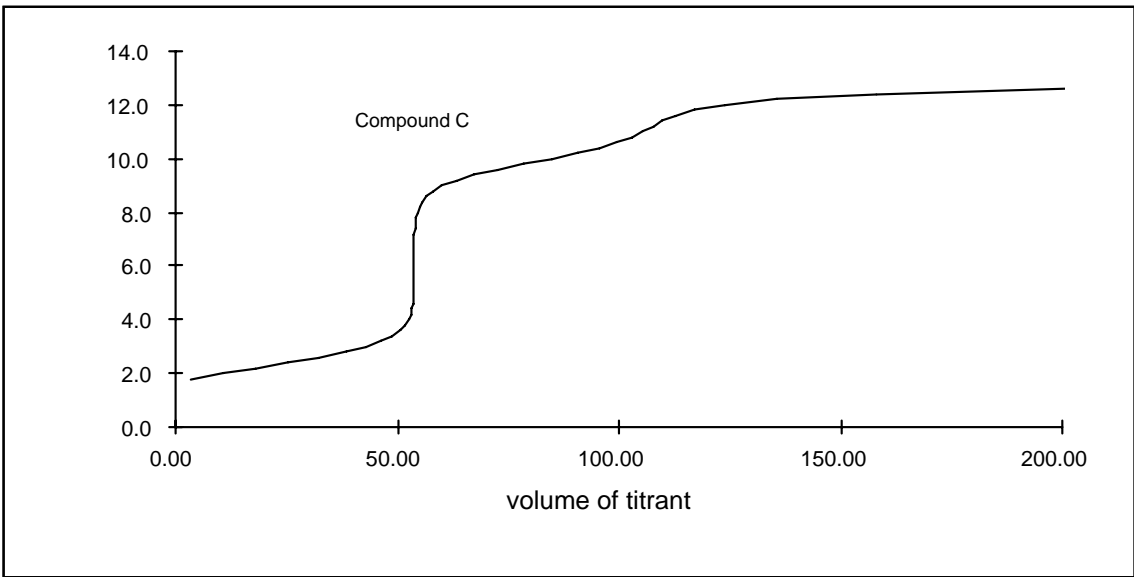
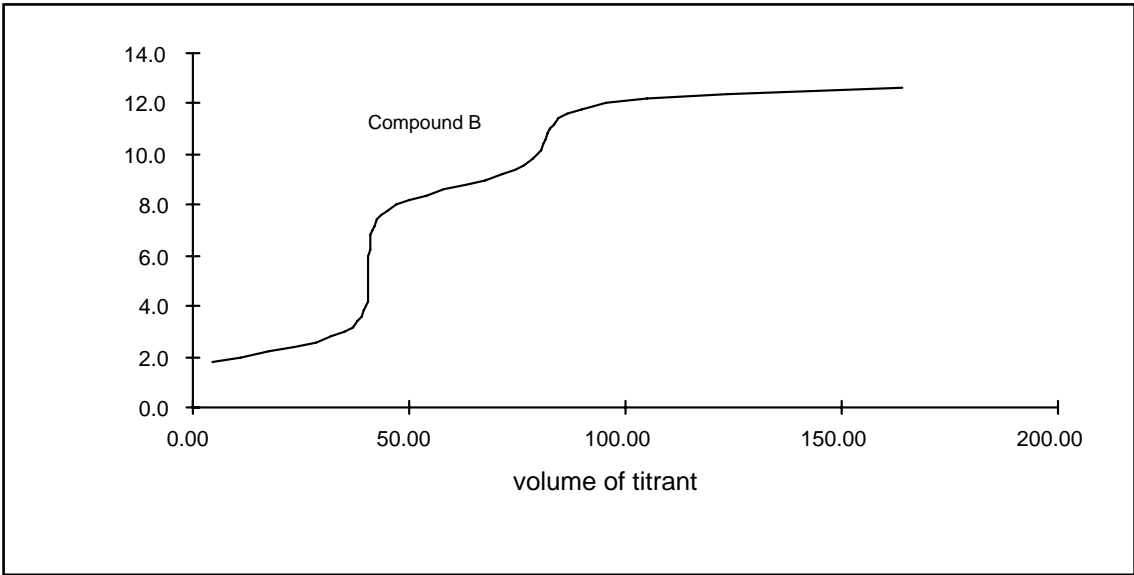
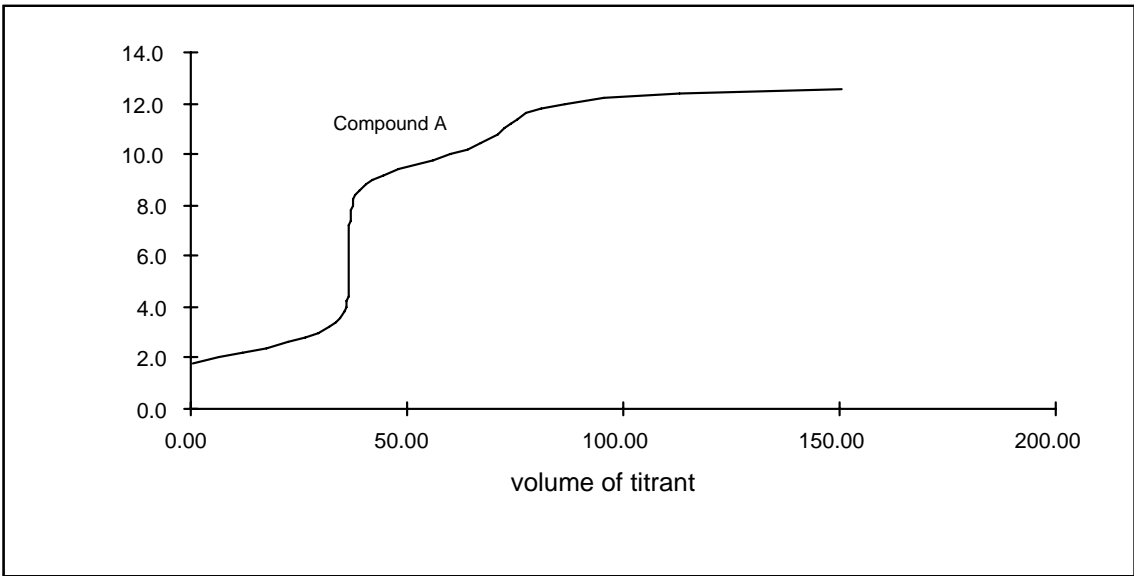
$$K_D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}}} \quad \text{and} \quad D = \frac{[\text{HA}]_{\text{org}}}{[\text{HA}]_{\text{aq}} + [\text{A}^-]_{\text{aq}}}$$

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)	$\text{p}K_{\text{a}1}$	$\text{p}K_{\text{a}2}$
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^+ .

There are several approaches that you might take here. The simplest is to note that the molar mass for alanine•HCl has the smallest molar mass, which means that a 0.500-g sample of this amino acid will have the greatest number of moles and will require the greatest volume of HCl to reach an equivalence point; thus, compound C must be alanine•HCl



3. The titrimetric analysis of amino acids is complicated by the high pK_a of the $-\text{NH}_4^+$ 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.

To complete a back-titration for a weak acid we add an excess of a standard strong base, such as NaOH. The NaOH completely consumes the weak acid and the remaining, unreacted NaOH is then titrated with a standard strong acid. This approach produces a better end point because the titration of a strong base with a strong acid gives a well-defined end point at a pH of 7 and with a significant break because the concentrations are kept high.

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], Vilchez and co-workers describe a spectrofluorometric method for the quantitative analysis of the antibiotic norfloxacin. In the paper, the authors note that the presence of 330 ng/mL Cu^{2+} in the presence of 2.0 ng/mL norfloxacin produces an error of +5%. What is the selectivity coefficient for the analysis of norfloxacin in the presence of Cu^{2+} ?

The signal from 300 ng/mL of Cu^{2+} is equivalent to 5% of the signal from 2.0 ng/mL norfloxacin; thus

$$(0.05)(2.0 \text{ ng/mL}) = K_{A,I}(300 \text{ ng/mL})$$

Solving gives $K_{A,I}$ as 3.0×10^{-4}

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?

They began with

$$(55.16 \times 10^{-3} \text{ mol/L}) \times 0.1 \text{ L} = 5.516 \times 10^{-3} \text{ mol AsCl}_3$$

in the aqueous phase and end up with

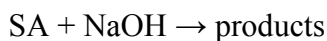
$$(17.65 \times 10^{-3} \text{ mol/L}) \times 0.1 \text{ L} = 1.765 \times 10^{-3} \text{ mol AsCl}_3$$

in the aqueous phase. The amount of AsCl_3 transferred to the ether phase is 3.751×10^{-3} moles. With a volume of 50.0 mL, the $[\text{AsCl}_3]_{\text{org}}$ is 7.50×10^{-2} M. The distribution ratio, therefore, is

$$D = [\text{AsCl}_3]_{\text{org}} / [\text{AsCl}_3]_{\text{aq}} = 7.50 \times 10^{-2} \text{ M} / 17.65 \times 10^{-3} \text{ M} = 4.25$$

3. Your company recently received a shipment of salicylic acid ($\text{C}_7\text{H}_6\text{O}_3$, 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).

Given the pK_a values for SA and the pH range for phenolphthalein's end point (8.3-10.0), the titration must occur to the first equivalence point; thus, the reaction is



and

$$(0.1354 \text{ M KOH}) \times (0.02192 \text{ L KOH}) \times \frac{1 \text{ mol SA}}{\text{mol KOH}} \times \frac{138.12 \text{ g SA}}{\text{mol SA}} = 0.4099 \text{ g SA}$$

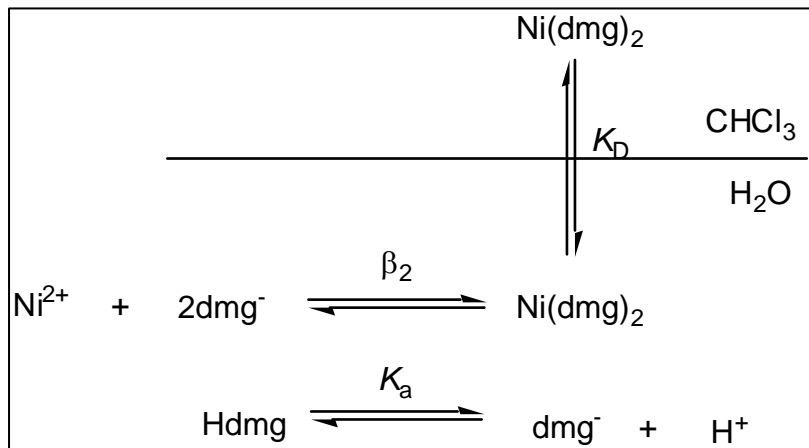
The %w/w salicylic acid is

$$\frac{0.4099 \text{ g SA}}{0.4208 \text{ g sample}} \times 100 = 97.4 \% \text{w/w}$$

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 dimethylglyoxime (dmg) as a complexing ligand. The relevant equilibria are shown to the right where K_D is 410, β_2 is 2.3×10^{17} , and K_a is 2.6×10^{-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 .

We begin with equations for D , β_2 and K_a ; thus

$$D = \frac{[\text{Ni}(\text{dmg})_2]_{\text{org}}}{[\text{Ni}^{2+}]_{\text{aq}} + [\text{Ni}(\text{dmg})_2]_{\text{aq}}} \quad \beta_2 = \frac{[\text{Ni}(\text{dmg})_2]_{\text{aq}}}{[\text{Ni}^{2+}]_{\text{aq}} [\text{dmg}^-]_{\text{aq}}^2} \quad K_a = \frac{[\text{dmg}^-]_{\text{aq}} [\text{H}^+]_{\text{aq}}}{[\text{Hdmg}]_{\text{aq}}}$$

Solving β_2 for $[\text{Ni}^{2+}]_{\text{aq}}$ and substituting into D gives

$$D = \frac{[\text{Ni}(\text{dmg})_2]_{\text{org}}}{\frac{[\text{Ni}(\text{dmg})_2]_{\text{aq}}}{\beta_2 [\text{dmg}^-]_{\text{aq}}^2} + [\text{Ni}(\text{dmg})_2]_{\text{aq}}} = \frac{[\text{Ni}(\text{dmg})_2]_{\text{org}}}{[\text{Ni}(\text{dmg})_2]_{\text{aq}} \left\{ \frac{1}{\beta_2 [\text{dmg}^-]_{\text{aq}}^2} + 1 \right\}} = \frac{K_D}{\frac{1}{\beta_2 [\text{dmg}^-]_{\text{aq}}^2} + 1}$$

Simplifying this gives

$$D = \frac{K_D \beta_2 [\text{dmg}^-]_{\text{aq}}^2}{1 + \beta_2 [\text{dmg}^-]_{\text{aq}}^2}$$

Finally, solving K_a for $[\text{dmg}^-]$ and substituting back gives

$$D = \frac{K_D \beta_2 K_a^2 [\text{Hdmg}]_{\text{aq}}^2 / [\text{H}^+]_{\text{aq}}^2}{1 + \beta_2 K_a^2 [\text{Hdmg}]_{\text{aq}}^2 / [\text{H}^+]_{\text{aq}}^2} = \frac{K_D \beta_2 K_a^2 [\text{Hdmg}]_{\text{aq}}^2}{[\text{H}^+]_{\text{aq}}^2 + \beta_2 K_a^2 [\text{Hdmg}]_{\text{aq}}^2}$$

The goal of the extraction is to recover the Ni^{2+} from its aqueous matrix. Calculate the extraction efficiency for $\text{Ni}(\text{dmg})_2$ 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.

Solving for the distribution ratio gives its value as 17.8. The value for q_{aq} is

$$\frac{50.0}{(17.8)(25.0) + 50.0} = 0.101$$

and the extraction efficiency is 89.9%.

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

To determine the number of extractions we set up the following relationship

$$0.001 = (0.101)^n$$

Solving for n gives its value as 3.01, which means that we need 4 extractions to achieve this recovery.

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.

Yes. If $[\text{H}^+]_{\text{aq}} \ll \beta_2 K_a^2 [\text{Hdmg}]_{\text{aq}}^2$ and $D = K_D$, which is the largest possible value for D. Another way to justify this is to note that making the pH more basic favors the conversion of Hdmg to dmg^- and favors the formation of $\text{Ni}(\text{dmg})_2$ and thus favors the extraction of $\text{Ni}(\text{dmg})_2$ into the organic phase.

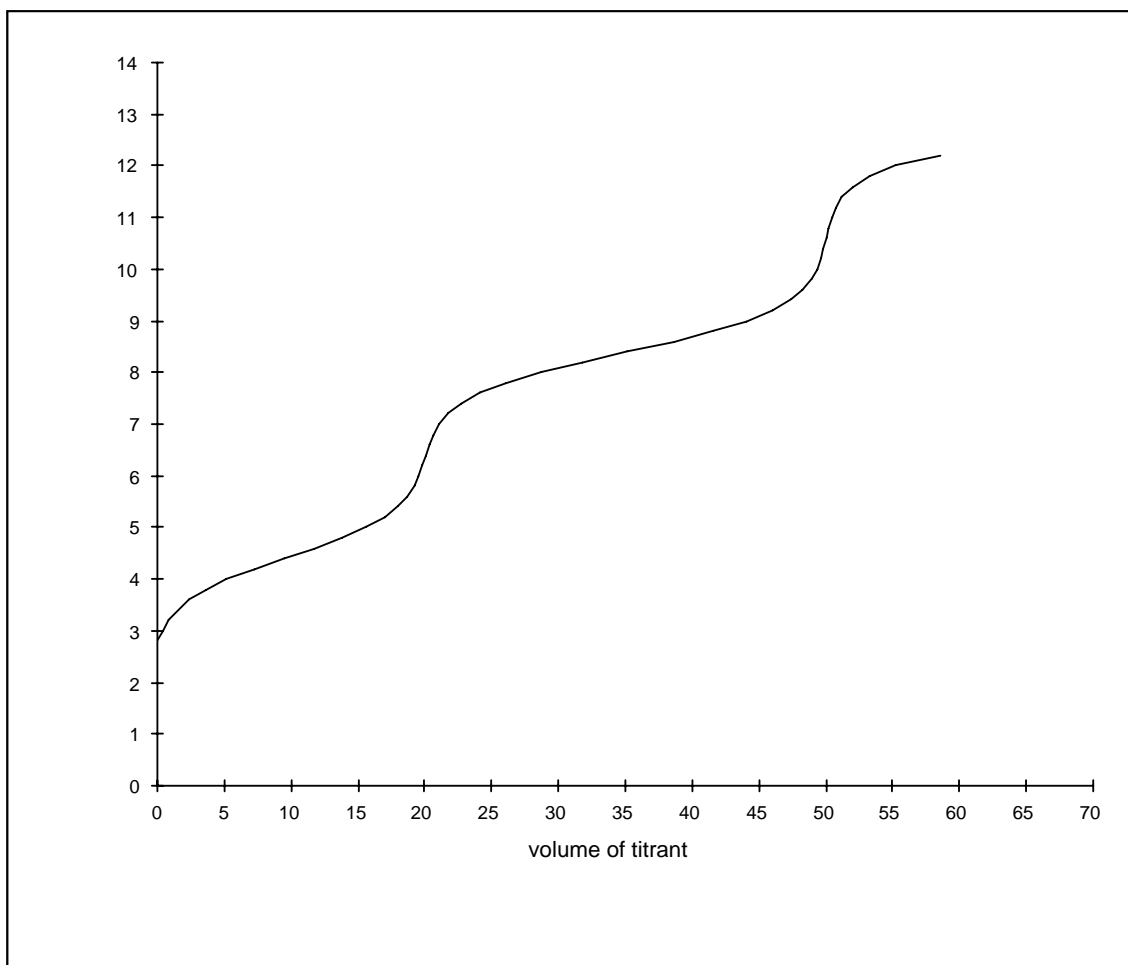
In addition to pH, identify at least one other way you could increase the recovery of Ni^{2+} in a single extraction. Briefly justify your choice with an appropriate explanation or calculation.

There are three other ways to effect a better recovery. You can increase V_{org} , you can decrease V_{aq} or you can increase the equilibrium value for $[\text{Hdmg}]_{\text{aq}}$. Each of these choices can be verified by working through an example 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.

The two equivalence points are at nominally 20 mL of titrant and 50 mL of titrant. If the titration was for a diprotic weak acid, then the second equivalence point would be exactly twice that for the first equivalence point, or 40 mL.

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

The first equivalence point is for 2-methylanilinium as it is the stronger of the two weak acids.

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

Bromocresol purple, which has a range of 5.2-6.8, is the best of the available indicators.

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?

It takes 30.0 mL of titrant to neutralize the analyte (the volume of titrant need to move from the first to the second equivalence point). The titration reaction is



and the mass of 3-nitrophenol in the sample is

$$(0.200 \text{ M NaOH}) \times (0.300 \text{ L NaOH}) \times \frac{1 \text{ mol 3 - NP}}{\text{mol NaOH}} \times \frac{139.1 \text{ g 3 - NP}}{\text{mol 3 - NP}} = 0.8346 \text{ g 3 - NP}$$

and the %w/w 3-nitrophenol is

$$\frac{0.8346 \text{ g 3 - NP}}{2.006 \text{ g sample}} \times 100 = 41.6 \% \text{w/w 3 - NP}$$

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.

Your sketch should show two small deviations. The initial pH will be slightly more basic because the concentrations of the weak acids are slightly smaller, and the pH after the second equivalence point will be slightly less basic because the excess titrant will be diluted to a greater extent. Note that the equivalence points are unchanged as the moles of each weak acid have not changed (just their concentrations, but chemical reactions occur on a mole-to-mole basis).

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