

Investigating an Acid Mixture

In this experiment you will determine the quantitative composition of a solution, which is a mixture of a strong acid, HCl, and a weak acid, H₃PO₄. After titrating the mixture with a standard NaOH solution, you will employ quantitative volumetric analysis to determine the molar concentrations of the acids in the mixture.

The strong acid in the mixture completely dissociates in water and the weak acid partially dissociates. The extent of the weak acid dissociation is represented by an equilibrium constant, K_a . The weak acid in your mixture is triprotic, thus its dissociation is described by three equilibrium constants. Understanding the behavior of the acids as they dissociate is a key component to evaluating the results of the titration.

OBJECTIVES

In this experiment, you will:

- Titrate a mixture of HCl and H₃PO₄ with standard NaOH solution.
- Calculate the molar concentration of each acid in the mixture.
- Calculate the K_{a2} (or pK_{a2}) for the weak acid.

MATERIALS

Vernier data-collection interface	0.100 M sodium hydroxide, NaOH solution
data-collection software	HCl/H ₃ PO ₄ mixture, unknown molarity
pH Sensor	distilled water
magnetic stirrer and stirring bar	glassware, clamps, and supplies as needed

PROCEDURE

1. Obtain and wear goggles.
2. Obtain a 30 mL sample of the unknown acid mixture and a volume of 0.100 M NaOH solution. **CAUTION:** *Handle the acid mixture with care. It can irritate the eyes and skin. Sodium hydroxide solution is caustic. Avoid spilling it on your skin or clothing.*
3. Set up the necessary pieces of equipment to titrate the acid mixture with 0.100 M NaOH solution. Plan your use of the acid mixture so that you can conduct at least two titration runs, keeping in mind that you have only 30 mL with which to work.
4. Set up either the Logger *Pro* 3 software or the LabQuest app to collect pH vs. volume data. Refer to previous titration lab instructions for help with the set up.
5. Conduct the titration. You may wish to conduct the first run in quick-and-dirty fashion, adding 1-2 mL of the NaOH solution at a time to see the general region (or regions) where the equivalence point occurs. One titration run should be done very carefully, to identify the volume of NaOH needed to reach an equivalence point.

DATA TABLE

Trial	Volume acid mixture (mL)	[NaOH] (M)	1st Equivalence point (mL)	2nd Equivalence point (mL)
1				
2				
3				

DATA ANALYSIS

1. How many moles of NaOH were used to reach the 1st and 2nd equivalence points?
2. What are the molar concentration of the HCl and the H₃PO₄ in the acid mixture? Explain how you calculated these values.
3. Use your titration data and the Henderson-Hasselbalch equation to calculate the K_{a2} for H₃PO₄. The literature value is 6.2×10^{-8} . How does your calculated K_{a2} compare with the literature value? For the generic dissociation: $\text{HX} \leftrightarrow \text{H}^+ + \text{X}^-$, a version of the Henderson-Hasselbalch equation is shown below.

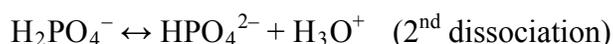
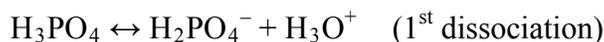
$$pH = pK_a + \log \frac{[\text{X}^-]}{[\text{HX}]}$$

DATA ANALYSIS NOTES

Dealing with a mixture of acids seems tricky at first glance. If, for example, you were to titrate a solution of only HCl or H₃PO₄, it would be a simple matter to determine the concentration of the acid and/or the dissociation constant, K_a, of the weak acid. However, when you titrate an aqueous solution containing both HCl and H₃PO₄ the task of determining much of anything about the mixture seems quite complex.

Until you think about equilibrium. Let's explore phosphoric acid in more detail.

A weak acid is all about equilibrium, and phosphoric acid (H₃PO₄) has a lot of equilibrium going on. This is what you get in an aqueous solution of H₃PO₄:



Now, when you mix some HCl with a solution of H₃PO₄, you are adding a huge amount of H₃O⁺ ions because HCl is a strong acid (dissociates completely). Recall what LeChatelier had to say about equilibria and you will see that the 1st dissociation equation contains a whole lot of H₃PO₄ and H₃O⁺ and practically no H₂PO₄⁻. This is what your acid mixture looks like before you start the titration.

As you titrate the mixture of HCl and H₃PO₄ with a sodium hydroxide solution, the OH⁻ ions react with H₃O⁺ ions from the HCl and the H₃PO₄ molecules to reach the 1st equivalence point. On the titration plot, however, there is no way to identify the source of the H₃O⁺ ions up to the 1st equivalence point. But, we'll be able to figure it out.

As the titration continues past the 1st equivalence point, you are now neutralizing the H₂PO₄⁻ ions. The number of moles of NaOH you add from the 1st eq. pt. to the 2nd eq. pt. is equal to the number of moles of H₂PO₄⁻ ion. Also, the original amount of H₃PO₄ in the mixture is equal to the moles of H₂PO₄⁻ ions (see the 1st dissociation equation). Thus, to calculate the number of moles of HCl in the mixture you subtract the moles of H₂PO₄⁻ from the moles of NaOH used to reach the 1st eq. pt. From here, calculating the molar concentration of HCl and H₃PO₄ is simple. That piece of the puzzle is solved.

How do we calculate the K_{a2} (or the pK_{a2}) of phosphoric acid? The equilibrium expression for the 2nd dissociation is shown below:

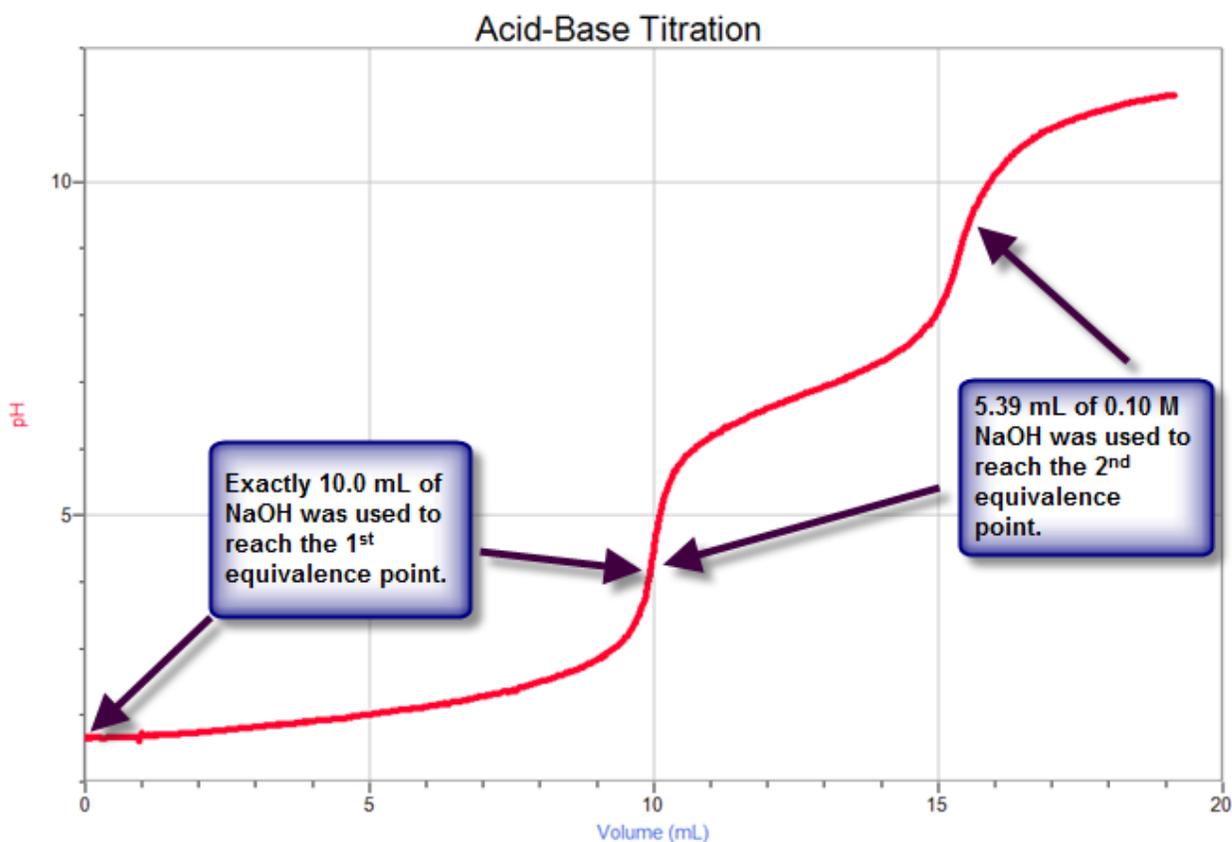
$$K_{a2} = \frac{[\text{HPO}_4^{2-}][\text{H}_3\text{O}^+]}{[\text{H}_2\text{PO}_4^-]}$$

If we take the logarithm of both sides of this equation, and do a bit of rearranging, we get the Henderson-Hasselbalch equation:

$$pK_{a2} = pH + \log \frac{[HPO_4^{2-}]}{[H_2PO_4^-]}$$

In this version of the Henderson-Hasselbalch equation, if the molar concentration of the two ionic species is equal then the pK_{a2} and the pH are equal. This event occurs exactly halfway between the 1st eq. pt. and the 2nd eq. pt. Thus, you can read the pK_{a2} of phosphoric acid directly from the titration plot.

Here's an example. The graph below shows the titration of 10.0 mL of a mixture of HCl and H_3PO_4 with 0.10 M NaOH solution.



$(0.00539 \text{ L}) \times (0.10 \text{ mol/L}) = 5.39 \times 10^{-4} \text{ mol}$ of OH^- used between 1st and 2nd eq. pts.
 $\therefore 5.39 \times 10^{-4} \text{ mol}$ of $H_2PO_4^-$ and $5.39 \times 10^{-4} \text{ mol}$ of H_3PO_4 were in the mixture
 $[H_3PO_4] = 5.39 \times 10^{-4} \text{ mol} \div 0.010 \text{ L of total mixture} = 0.00539 \text{ M}$

$(0.010 \text{ L}) \times (0.10 \text{ mol/L}) = 0.0010 \text{ mol}$ of OH^- used to reach the 1st eq. pt.
 $\therefore 0.0010 \text{ mol}$ of H_3O^+ ions came from $HCl + H_3PO_4$
 ...and, we know that there were $5.39 \times 10^{-4} \text{ mol}$ of H_3PO_4
 $\therefore \text{mol HCl} = 0.0010 \text{ mol} - 5.39 \times 10^{-4} \text{ mol} = 4.61 \times 10^{-4} \text{ mol}$
 $[HCl] = 4.61 \times 10^{-4} \text{ mol} \div 0.010 \text{ L of total mixture} = 0.00461 \text{ M}$

Examine another region of the titration plot to determine the pK_{a2} of H_3PO_4 .

