Department of Chemistry
University of Texas at Austin
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## Aqueous Equilibria Unit Activity - Discovering the Titration Curve KEY

The purpose of running a titration experiment and plotting a pH curve is to find the equivalence point of an acid base neutralization reaction such that one can determine the concentration of an acid or base; or to determine the Ka of a weak acid or the Kb of a weak base. Use the data in the tables below to answer the associated questions, such that you might come to understand the point of titration curves.

1. What are the primary purposes for doing a $\mathbf{p H}$ titration?

The primary purposes are: to find concentration of an acid or base, to figure out the Ka or Kb of a species. We determine these values by looking for the equivalence point of a titration.

Some useful background information: The equivalence point is the point at which the number of moles of added base (or acid) equals the number of moles of acidic protons (or moles of base) that are in the solution to which the base (or acid) is being added. The concentration of the solution, called the "titrant", which is being carefully dripped into the "unknown" solution- the analyte, is known to great accuracy. The purpose of dripping the titrant into the analyte solution is to determine the concentration of the acid (or base) in the unknown solution. One can use the data from a titration experiment to determine this equivalence point because there will be a sharp rise (or fall, depending on the type of titration) in pH once the neutralization of the acid (or base) has been completed.
PART I - TITRATION OF A STRONG ACID WITH A STRONG BASE
The following data is from a titration in which 0.1 M NaOH is slowly added to 100 mL HBr of unknown concentration.
5 min to work on this. Then ask some what they got for pH .

| Total Volume NaOH <br> added | Total \# moles OH <br> added to solution | pH | Dominant <br> Species |
| :---: | :---: | :---: | :---: |
| 0 mL | 0.0 mmol |  | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| 5 mL | 0.5 mmol | 2.70 | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| 6 mL | 0.6 mmol | 3.00 | $\mathrm{H}_{3} \mathrm{O}^{+}$ |
| 7 mL | 0.7 mmol | 7.00 | neither |
| 10 mL | 1.0 mmol | 11.48 | $\mathrm{OH}^{-}$ |
| 11 mL | 1.1 mmol | 11.60 | $\mathrm{OH}^{-}$ |
| 13 mL | 1.3 mmol | 11.78 | $\mathrm{OH}^{-}$ |

Fill in the remaining numbers in the center column of the table.
$\mathrm{M}^{*} \mathrm{~V}=\mathrm{mol} \quad \mathrm{EX}:(0.1 \mathrm{M})(5 \mathrm{~mL})=(0.1 \mathrm{M})(0.005 \mathrm{~L})=0.0005 \mathrm{~mol}=0.5 \mathrm{mmol}$
2. For each row state if $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$is the dominant species.

Use the pH to help you here. If the pH is less than 7, the dominant species must be $\mathrm{H}_{3} \mathrm{O}^{+}$. If the pH is greater than 7 , the dominant species must be $\mathrm{OH}^{-}$. If the pH is exactly 7 , then neither species is dominant because they are equal in concentration.
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3. Use the data in the table to determine the initial number of moles of $\mathrm{H}_{3} \mathrm{O}^{+}$in the solution before the addition of NaOH .

The equivalence point is the point at which the moles of base exactly equal the moles of acid. We know (because we are good chemists) that HBr is a strong acid and NaOH is a strong base. When combined in equal molar amounts, they will create a neutral solution.

We can see that the solution is neutral and that neither $\mathrm{H}_{3} \mathrm{O}^{+}$or $\mathrm{OH}^{-}$is dominant when 7 mL of NaOH has been added. In this titration with 0.1 M base, 7 mL of added NaOH means 0.7 mmol of base had been added.

The equivalence point occurs when 0.7 mmol of base has been added which means it must have reacted exactly with 0.7 mmol of acid! $\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=\left[\mathrm{OH}^{-}\right]$
pH 7 when $[\mathrm{HBr}]=[\mathrm{NaOH}]$. This occurs when 0.7 mmol NaOH , so 0.7 mmol HBr
4. Use the data in the table to determine the concentration of the initial HBr solution. Clicker question
We know that 0.7 mmol of acid must have been present because the solution reached the equivalence point when 0.7 mmol of base were added. Initially, before base was added, those 0.7 mmol of HBr were floating around in 100 mL of solution.
$M=(\mathrm{mol}) /(\mathrm{L})=\left(0.7 \times 10^{-3} \mathrm{~mol}\right) /(0.100 \mathrm{~L})=0.007 \mathrm{M}$ solution of HBr
Now we could determine the pH of the original solution if we wanted! The HBr would be completed dissociated in solution. So the concentration of $\mathrm{H}_{3} \mathrm{O}^{+}$would be equal to the concentration of the acid itself ( $1: 1$ ration for HBr ).
$\mathrm{pH}=-\log \left[\mathrm{H}_{3} \mathrm{O}^{+}\right]=-\log (0.007)=2.15$
We would put 2.15 in the first blank in the pH column before any base has been added.

## PART II - TITRATION OF A WEAK ACID WITH A WEAK BASE

The following data is from a titration of 100 mL of acetic acid with a sodium hydroxide. The concentration of the strong base is known. Study this data table, then answer the questions.

1. Write down the neutralization reaction that is occurring here:

$$
\mathrm{CH}_{3} \mathrm{COOH}(\mathrm{aq})+\mathrm{NaOH}(\mathrm{aq}) \rightarrow \mathrm{CH}_{3} \mathrm{COO}^{-}(\mathrm{aq})+\mathrm{Na}^{+}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(\mathrm{l})
$$

| Total <br> Volume <br> NaOH <br> added | Total \# <br> moles <br> $\mathrm{OH}^{-}$ <br> added to <br> solution | \# moles after Neutralization <br> mmol |  |  | Measured <br> pH | "type" of <br> solution |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
|  |  | $\mathrm{CH}_{3} \mathrm{COOH}$ | $\mathrm{CH}_{3} \mathrm{COO}^{-}$ | $\mathrm{OH}^{-}$ |  |  |
| 0 mL | 0.0 mmol | 0.8 | 0 | 0 | 3.437 | Weak Acid |
| 2 mL | 0.2 mmol | 0.6 | 0.2 | 0 | 4.295 | Buffer*** |
| 3 mL | 0.3 mmol | 0.5 | 0.3 | 0 | 4.542 | Buffer |
| 4 mL | 0.4 mmol | 0.4 | 0.4 | 0 | 4.761 | Buffer |

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| 5 mL | 0.5 mmol | 0.3 | 0.5 | 0 | 4.981 | Buffer |
| :---: | :---: | :---: | :---: | :---: | :---: | :---: |
| 6 mL | 0.6 mmol | 0.2 | 0.6 | 0 | 5.236 | Buffer |
| 7 mL | 0.7 mmol | 0.1 | 0.7 | 0 | 5.603 | Buffer |
| 8 mL | 0.8 mmol | 0.0 | 0.8 | 0 | 8.312 | Weak Base |
| 9 mL | 0.9 mmol | 0.0 | 0.8 | 0.1 | 10.96 | Strong Base |
| 10 mL | 1.0 mmol | 0.0 | 0.8 | 0.2 | 11.257 | Strong Base |

***When there is a mixture of a conjugate acid and base pairs such as $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COO}^{-}$we call this solution a buffer. As long as the two species have concentrations similar in magnitude (like these here) we can consider the solution a buffer.

Fill in the remaining data points in the table.
2. What has to be true about the sum of the numbers of moles of $\mathrm{CH}_{3} \mathrm{COOH}$ and $\mathrm{CH}_{3} \mathrm{COO}$ - for all the solutions?
The sum of the number of moles of the acid and its conjugate base must be constant. As we add base we make the conjugate base from the acid. So we are not mysteriously creating moles of a species out of thin air, but rather converting the moles of acid into the moles of conjugate base.
3. For each solution, describe what type of equilibrium best describes the species in that solution (strong acid, weak acid, buffer, weak base, strong base).
See Table
4. What is the pKa for acetic acid based on the data? What is the Ka?

Clicker question
The $\mathrm{pK}_{\mathrm{a}}$ is equal to the pH when the acid and its conjugate base are present in equimolar amounts in solution!

$$
\begin{gathered}
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log \left(\left[\mathrm{A}^{-}\right] /[\mathrm{HA}]\right) \\
{[\mathrm{A}]=[\mathrm{HA}]} \\
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+\log (1) \\
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}+0 \\
\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}
\end{gathered}
$$

In our situation, when 0.4 mmol of NaOH has been added, then 0.4 mmol of $\mathrm{CH}_{3} \mathrm{COOH}$ are present with 0.4 mmol of $\mathrm{CH}_{3} \mathrm{COO}^{-}$. The pH of the solution at this point is equal to the $\mathrm{pK}_{\mathrm{a}}$. So the $\mathrm{pK}_{\mathrm{a}}$ must be 4.761 .
$\mathrm{pK}_{\mathrm{a}}=-\log \left(\mathrm{K}_{\mathrm{a}}\right)$
$4.761=-\log \left(\mathrm{K}_{\mathrm{a}}\right)$
$10^{-4.761}=\mathrm{K}_{\mathrm{a}}$
$1.7 \times 10^{-5}=K_{a}$
5. What is volume of added NaOH at the end point? Is there something special when $1 / 2$ this volume is added?
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When 8 mL have been added, all of the acetic acid $\mathrm{CH}_{3} \mathrm{COOH}$ has been converted to its conjugate base $\mathrm{CH}_{3} \mathrm{COO}^{-}$. This is known as the equivalence point.

At half this point, there are equal amounts of the weak acid and its conjugate base, where the $\mathrm{pH}=\mathrm{pK}_{\mathrm{a}}$. We can find the $\mathrm{pK}_{\mathrm{a}}$, and therefore the $\mathrm{K}_{\mathrm{a}}$ at half of the equivalence point.

## 6. What was the concentration of the initial acetic acid solution?

Clicker question
Initially, there were 0.8 mmol in 100 mL .
0.0008 moles in 0.1 L
$\frac{0.0008 \text { moles }}{0.1 \mathrm{~L}}=0.008 \mathrm{M}$
Or, 8 mM
7. Summarize here what you have learned from this activity: specifically explain how can one use titration to determine the Ka of a weak acid.

It is possible to determine the Ka of a weak acid by titrating in a known amount of a strong base. By taking careful measurements, one can determine the equivalence point, where the amount of added strong base has neutralized all of the weak acid.

Once this equivalence point has been found, half of this amount, the point at which half of the weak acid has been converted to its conjugate base, when there are equal amounts of weak acid and conjugate base, is where the $\mathrm{pH}=\mathrm{pKa}$.

