

Strong Acid/Strong Base Titrations:

As with all titrations, those that involve only strong acids and strong bases have 4 distinct regions. Since the pH of an acid or base solution indicates the concentration of hydronium ion and the acidity of the solution, it is usually calculated or experimentally determined as we add titrant. The ubiquitous use of pH meters these days also makes it important that we learn methods to calculate the pH for the titration of an acid or a base. The volume range for each region is determined by the position of the equivalence point volume, and this quantity should be the first that is determined. You should review these concepts in your textbook: 1) Bronsted-Lowry acids and bases, 2) Lewis Acids and Bases, 3) autoprotolysis of water, and 4) the pH/pOH scale.

The typical titration curve plots the p function of a species (in this case pH) versus volume of titrant added. It is usually sigmoidal in shape. A large change in concentration of the analyte species at the equivalence point causes the p function to abruptly change. It is this change that we detect either by recording the pH versus titrant (derivative to detect the change) or by using a visual indicator. The change in the p function at the equivalence point should be almost instantaneous have an infinite slope. Gradual changes in the p function nearing the equivalence point can still be used, but the uncertainty in the position of the equivalence point volume is increased. This is why we study and calculate titrations curves. In the curve of Figure 1, we can see the effect of the starting concentration of the acid on the shape of the curve and the sharpness of the inflection point. The first inflection point is not as clear as the second.

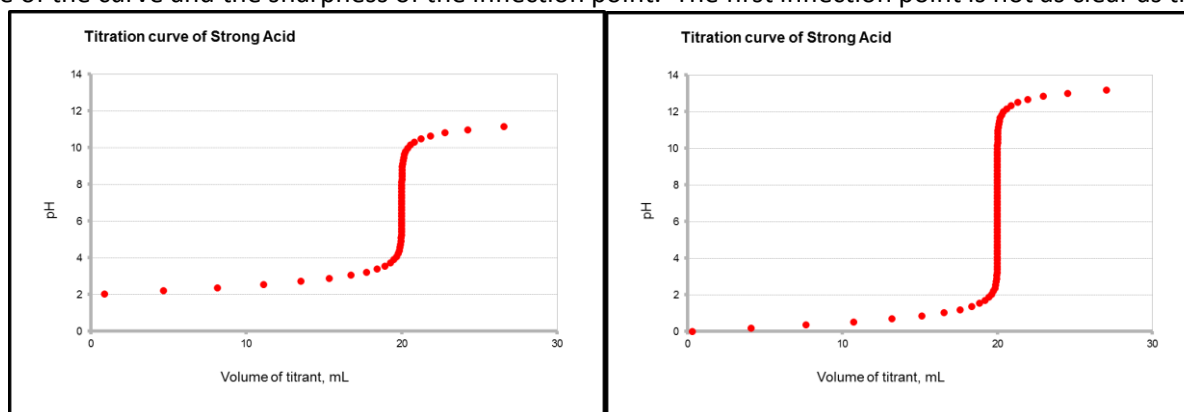
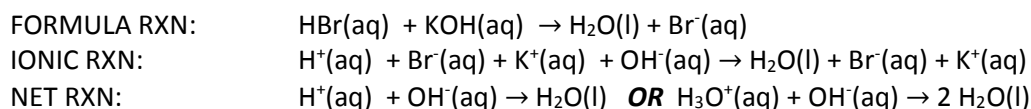


Figure 1: 20.00 mL of an HCl solution is titrated with base in both plots. In the left plot $c_{\text{HCl}} = 0.010 \text{ F}$ and $c_{\text{NaOH}} = 0.0100 \text{ F}$ and in the right plot $c_{\text{HCl}} = 1.00 \text{ F}$ and $c_{\text{NaOH}} = 1.00 \text{ F}$.

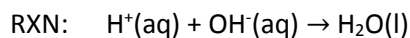
To keep it simple, let's consider the titration of 10.00 mL of a 0.100 F hydrobromic acid solution with 0.200 F potassium hydroxide. The reaction is:



These reactions say that for the most part, we do not need to worry about any equilibrium considerations. This is a reaction between a strong acid and a strong base and these always go to completion because hydronium ion directly reaction with hydroxide. The only time we have to worry about equilibria is when we have neutralized the acid (or base as the vase may be). At that point autoprotolysis of water determine the pH. Also remember that hydronium and hydroxide ion are the strongest acid and base, respectively, that can exist in an aqueous solution.

The acid is the analyte and the base is the titrant. Let's examine the chemistry in the four regions so we can calculate the pH as titrant is added. But first we need to know the equivalence point volume.

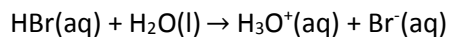
- Q1. Find the equivalence point volume, in mL, for this titration: 10.00 mL of a 0.100 F hydrobromic acid solution is titrated with 0.200 F potassium hydroxide.



Region #1: Initial (0 mL titrant added)

Finding the pH (analyte)

Since titrant has not been added, the initial analyte solution has a known composition. Hydrobromic acid is a strong acid which completely dissociates in solution:

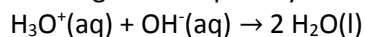


The concentration of hydronium and bromide ion are the same here: 0.100 M.

- Q2: Find the pH of this solution (use correct significant figures!)

$$\text{pH} = -\log[\text{H}_3\text{O}^+] = \underline{\hspace{2cm}}$$

- Q3: The equilibria governing the autoprotolysis of water is



Write the expression for the thermodynamic equilibrium constant, K_w .

- Q4: Based on your answer to Q2, find the hydroxide ion concentration and the pOH.

$$[\text{OH}^-] = \underline{\hspace{2cm}}$$

$$\text{pOH} = \underline{\hspace{2cm}}$$

- Q5: You should confirm that $\text{pH} + \text{pOH} = 14$ at 25°C.

Region #2: Pre-Equivalence ($0 < \text{Volume Titrant Added} < \text{Equivalent Point Volume}$)

In this region, we have added a volume of base which is greater than 0, but less than the equivalence point volume (see Q1). The titrant will ALWAYS be the limiting reagent in this case, and the analyte concentration will be determined as the difference between what we started out with and what was lost. We use an ICF chart to find the concentration of the excess analyte. ICF charts are helpful when you have a reaction that goes to completion.

Q5: Calculate the number of millimoles of hydronium ion we start in the analyte solution. In the ICF chart below, enter this value in the initial column for the hydronium ion.

Q6: If we add 3.00 mL of the potassium hydroxide solution, find the millimoles of hydroxide ion added. Enter this value in the initial column for the hydroxide ion in the ICF chart.

Enter 0 millimoles for the initial amount of water formed in the ICF chart.

	$\text{H}_3\text{O}^+(\text{aq})$	$\text{OH}^-(\text{aq})$	\rightleftharpoons	$2 \text{H}_2\text{O}(\text{l})$
Initial				
Change				
Final				

Q7: Without doing any more calculations, explain how you know that the hydroxide ion is the limiting reagent.

Q8: Write the change in the number of millimoles based on the answer to Q7 and enter those values in the chart.

Q9: Determine the Final number of millimoles of each reactant and product left after the reaction completes.

Q10: a. Find the molar concentration of hydronium in the solution and the final pH after the addition of KOH.

$$[H_3O^+] =$$

b. Now that we have done the basic limiting reagent calculation, you also find the concentration of hydronium left over by using the following equation:

$$[H_3O^+] = \left(\frac{V_e - V_t}{V_e} \right) c_a \left(\frac{V_a}{V_a + V_t} \right)$$

Where V_e is the equivalence point volume, V_t is the volume of titrant you have added *before* the equivalence point, c_a is the original analytical concentration of the acid and V_a is the volume of the acid used. The term $\left(\frac{V_e - V_t}{V_e} \right)$ calculates the percentage of the analyte left and the term $\left(\frac{V_a}{V_a + V_t} \right)$ is the dilution factor.

$$[H_3O^+] =$$

$$pH =$$

Q11: What is the pH after the addition of 4.00 mL of the potassium hydroxide?

Other pre-equivalence point pH (and pOH) values can be found in a similar manner.

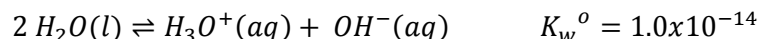
Region #3: Equivalence (Volume Titrant Added = Equivalent Point Volume)

Here we have added a volume of titrant that has reacted with ALL of the analyte in the solution (a stoichiometric amount). Both analyte and titrant are limiting in this case. We use an ICF chart to confirm these facts.

Q12: Fill in the ICF chart for the addition of 5.00 mL of potassium hydroxide titrant:

	$H^+(aq)$	$OH^-(aq)$	\rightleftharpoons	$H_2O(l)$
Initial				
Change				
Final				

After the addition of this volume of base, the acid analyte is completely neutralized. The analyte solution now has the soluble salt potassium chloride, KCl, and pure water. In this case, the autoprotolysis of water takes over and controls the pH of the solution:



Q13: Use the Final row of the ICF chart above to populate the Initial concentration row for the ICE chart for the autoprotolysis of water.

	2 H ₂ O(l)	⇌	H ₃ O ⁺ (aq)	OH ⁻ (aq)
Initial				
Change				
Equilibrium				

Q14: Write the change in concentration of each species in terms of the variable 'x' and enter then in the ICE chart's change row.

Q15: Write expression in terms of 'x' for each species at equilibrium by enter them in the ICE chart's equilibrium row.

Q16: Write the expression for $K_w^o =$ _____

Q18: Assuming that the ionic strength is close to 0 and activity coefficients are close to 1, find the value of 'x' if $K_w^o = 1.0 \times 10^{-14}$.

x =

Therefore, $[H_3O^+] = [OH^-] =$

Q19: Find the pH and pOH at the equivalence point.

pH =

pOH =

Q20: How will the presence of the salt, KCl, affect the pH at this point? Consider how the ionic strength will affect the activity and activity coefficient of the hydronium ion. Also remember that the true deficiency of pH is $-\log \mathcal{A}_{H_3O^+}$.

Region #4: Post-Equivalence (Volume Titrant Added > Equivalent Point Volume)

In this region, we have added a volume which is greater than the equivalence point volume (5.00 mL). By definition, the titrant is in excess and the analyte is now the limiting reagent. We basically have to figure out how much excess titrant we have, and this is easy to do since we know how the quantity of hydronium ion we started with and the quantity of hydroxide ion we have added. Again, we will use an ICF chart to find the concentration of the excess titrant.

Q21: Fill in the millimoles of each species present in the initial row for this ICF chart after the addition of 7.00 mL of the potassium hydroxide titrant:

	H ⁺ (aq)	OH ⁻ (aq)	⇌	H ₂ O(l)
Initial				
Change				
Final				

Q22: What species controls the pH of the solution post-equivalence. Explain.

Q23: Find the hydroxide ion concentration in the solution.

We can also use this equation to find the concentration of excess titrant: $[OH^-] = \frac{(V_t - V_e)c_t}{V_a + V_t}$ where V_t is the volume of titrant added past the equivalence point, V_e is the equivalence point volume, V_t is the titrant volume and c_t is the concentration of the titrant.

Q24: Find the pH and pOH of the solution.

pOH =

pH =

Q25: Build an EXCEL worksheet where you make a place for the user to enter the volume of acid titrated, the molarity of the acid and the molarity of the base titrant. Keep the stoichiometry 1:1 between the analyte and titrant.

Q26: Use this data to calculate and label two cells one that calculate the millimoles of acid initially present and another that contains the equivalence point (in mL).

Q27: Create a column called 'Percent Titrated,' and fill it with values from 0 to 120 incremented in steps of 1. You can use the Fill function to do this quickly.

Q28: In the column to the right of the one you just created, use the percent titrated value to calculate the volume of titrant added at that point in mL.

Q29: You have 4 regions, add columns to calculate the millimoles of base added and the millimoles of acid left.

Q30: You can now calculate the hydronium ion concentration for the initial and pre-equivalence points. You know what the pH at the equivalence point is already. No need to calculate it.

Q31: You will have to change you calculation for pH post equivalence, but have the data to do it.

Q32: Plot the data (pH versus volume of titrant).

You can now change the starting variables and see what happens to the curve. You should do this as part of your studies.