

Delving into Titrations Using ChemReaX™

A tutorial from [ScienceBySimulation](#)

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Introduction

In this article, we will use our free online chemistry simulation app, [ChemReaX](#), to examine titrations at a fine-grained level of detail to demonstrate how simulated titrations in a virtual lab can help students gain deep insights into the underlying reaction mechanism. With these insights from running simulated titrations with different molarities and volumes of the titrand and titrant, students can make the connections between theory and practice.

We will start with titrating a variety of acids as titrands against a strong base as a titrant to see the differences between strong and weak acids, and the differences between monoprotic and polyprotic acids. We will then look at one case where the hydrolysis reaction has a significant impact on the titration results.

Brief Theory of Titration in a Virtual Lab Context¹

An acid-base titration is typically used in a laboratory to determine the concentration of an acid or base (the titrand) by exactly neutralizing it with a strong acid or base (the titrant) of known concentration. Since the molarity of both the acid and base are known beforehand in a virtual lab, our focus will be on understanding the behavior of the neutralization reactions in detail. Incremental amounts of the titrant are added to a given amount of the titrand, and pH is measured at each increment after the solution reaches equilibrium. The result is plotted as the pH of the solution as a function of the titrant added. The end point or equivalence point of a titration is the region of steepest rise/fall in pH, where the titrant has exactly neutralized the titrand. Either the titrand or the titrant will be a limiting reagent in these reactions. Titration involves an acid-base equilibrium at each increment of the titrant volume, where two competing simultaneous equilibria must be accounted for: the ionization of the titrand (which could be a strong/weak acid or base) and the water autoionization. The final H(+) and OH(-) concentrations -- and the pH -- at each titrant increment are an outcome of resolving these simultaneous equilibria.

An additional adjustment to the pH must be made for the hydrolysis of water by the salts produced by the neutralization of weak acids/bases. The conjugate acid or base produced by the neutralization can extract an OH- or H+ from water to form the original weak base/acid and release additional H+ or OH- into the solution. As a result, aqueous solutions of salts of weak acids are basic, and aqueous solutions of salts of weak bases are acidic. Hydrolysis basically accelerates the pH change as the titration approaches the equivalence point.

In the case of polyprotic acids (strong or weak acids with more than one H+ to lose), there are multiple equivalence points corresponding to multiple ionizations. ChemReaX simulates only the first two ionizations of such acids, and ignores any additional ionizations. Hydrolysis is simulated for both ionizations, but omitted for clarity in any ionization where the equilibrium constant is less than $1e-9$. The second ionization is assumed to start once the first H+ from the acid has been completely neutralized,

¹ The theory in this section is based on Dill (2008).

which is a reasonable assumption if the equilibrium constant of the first ionization is much greater than that of the second ionization (such that as each individual proton in the aqueous solution is neutralized by the base, the first ionization will preferentially supply the next proton). Note that a relatively strong second ionization can depress the pH at the end of the first ionization to well below the neutral value of 7.

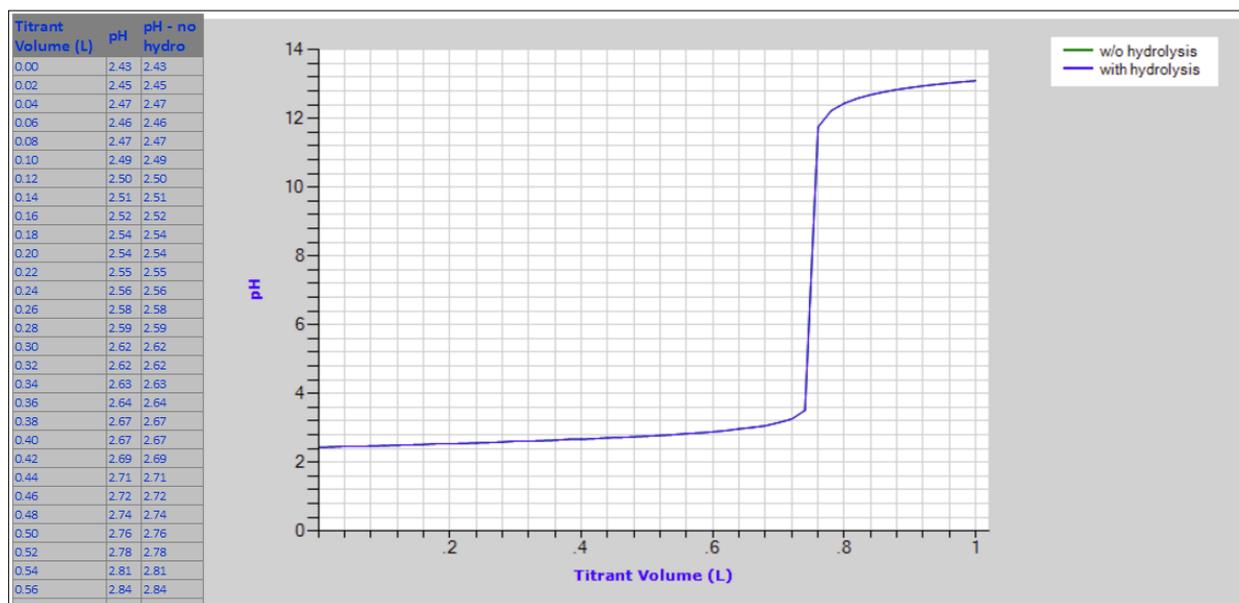
Running Titration Simulations

A typical acid-base titration with acid as titrand and base as titrant can be setup in ChemReaX as shown in the dashboard below. The variables include: the initial volume of the titrand, the molarity of the titrand, the total amount of titrand to be added to the solution in increments, and the molarity of the titrant. When the reaction is run by clicking "Run the Reaction", ChemReaX displays the entire series of reactions including any second ionization (none in this case) and the hydrolysis reaction. The simulated titration results generated by ChemReaX are shown at the bottom. The equivalence point occurs when the titrant volume is 0.75L as expected for the given concentrations.

Select Reactants	Species	Type	Initial Volume (L)	Total Amount Added (L)	Concentration (moles/L)	Equilibrium Constant, K
Analyte/Titrand	CH3CO2H	Weak Acid	1		0.75	1.75E-05
Reagent/Titrant	NaOH	Strong Base		1	1	100000

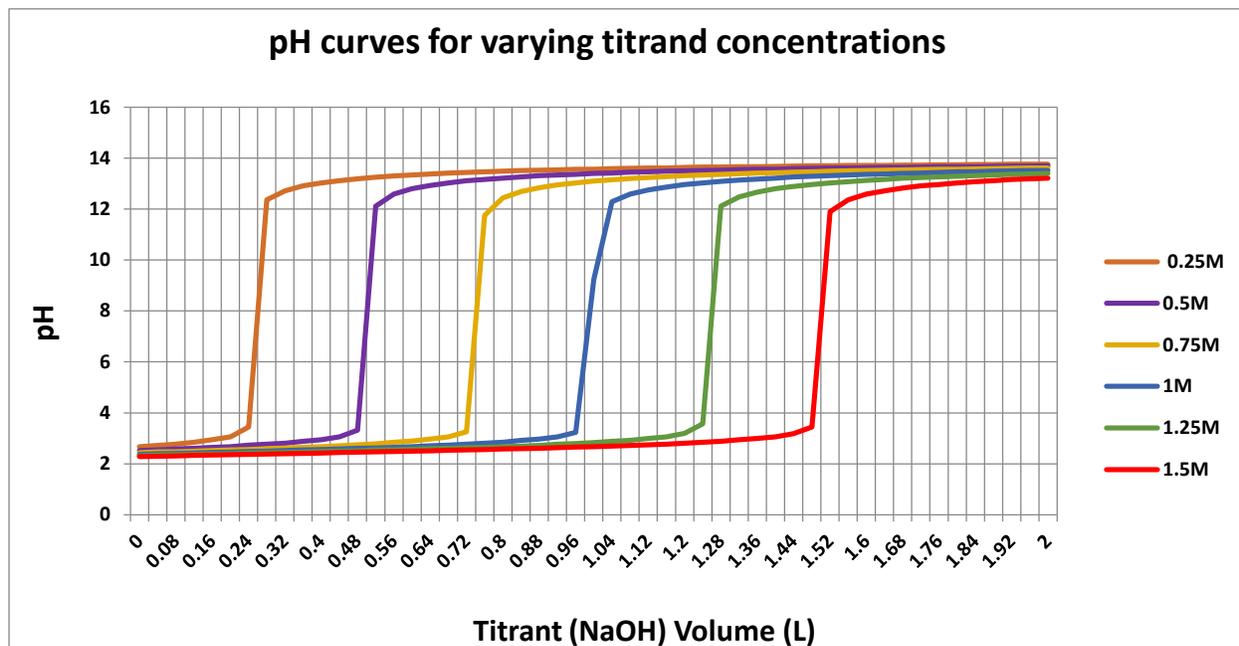
Reactions:

Titrand 1 st ionization:	CH3CO2H [aq]	+	<-->	H(+) [aq]	+	CH3CO2(-) [aq]
Titrand 2 nd ionization:	n/a	+	<-->		+	
Titrant ionization:	NaOH [aq]	+	---->	Na(+) [aq]	+	OH(-) [aq]
Water autoionization:	H2O [liquid]	+	<-->	H(+) [aq]	+	OH(-) [aq]
Hydrolysis:	H2O [liquid]	+	<-->	CH3CO2(-) [aq]	+	OH(-) [aq]
Hydrolysis:	n/a	+	<-->	CH3CO2H [aq]	+	



Varying the Titrand Concentrations

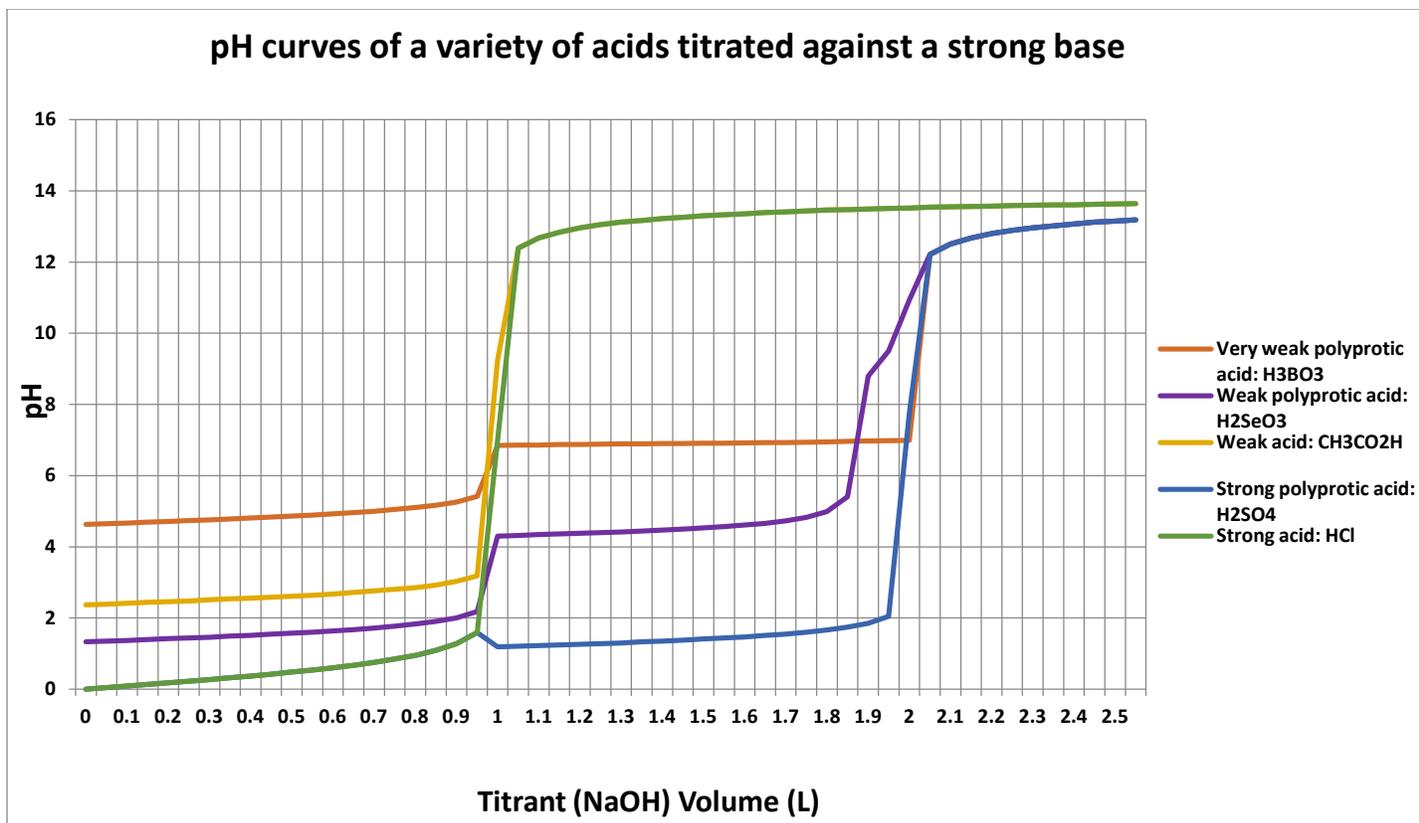
If we now re-run the above titration simulation with varying titrand concentrations, keeping the titrand volume at 1L and allowing the titrant volume to go up to 2L, we can see the equivalence point moving to the right as the titrand concentration increases. The chart below depicts this visually based on the data gathered from multiple titration simulations in ChemReaX.



Varying the Titrand Properties

Next, if we run similar simulated titrations of a different types of acids as titrands – including both strong and weak acids, and both monoprotic and polyprotic acids – against the same strong base as titrant (with all molarities set to 1M and the titrand volume set to 1L), the resulting data from the ChemReaX results table can be graphed in Excel as shown below. A few trends clearly emerge from this graph:

- Weaker acids start with a pH significantly higher than 0 – the weaker the acid, the higher the initial pH.
- The acid is neutralized by the titrant when the volume of the titrant is approximately 1L, which is as expected since the molarities of both the acid and the base are 1M in our example.
- The polyprotic acids undergo a second ionization after the first proton has been neutralized by the titrant. This second ionization is neutralized by the base approximately when the titrant volume is 2L as expected.
- Hydrolysis does shift the equivalence point as will be seen in more detail in the next section.



Bases can of course be used as titrands and acids as titrants, which would invert the pH curves seen above.

Hydrolysis

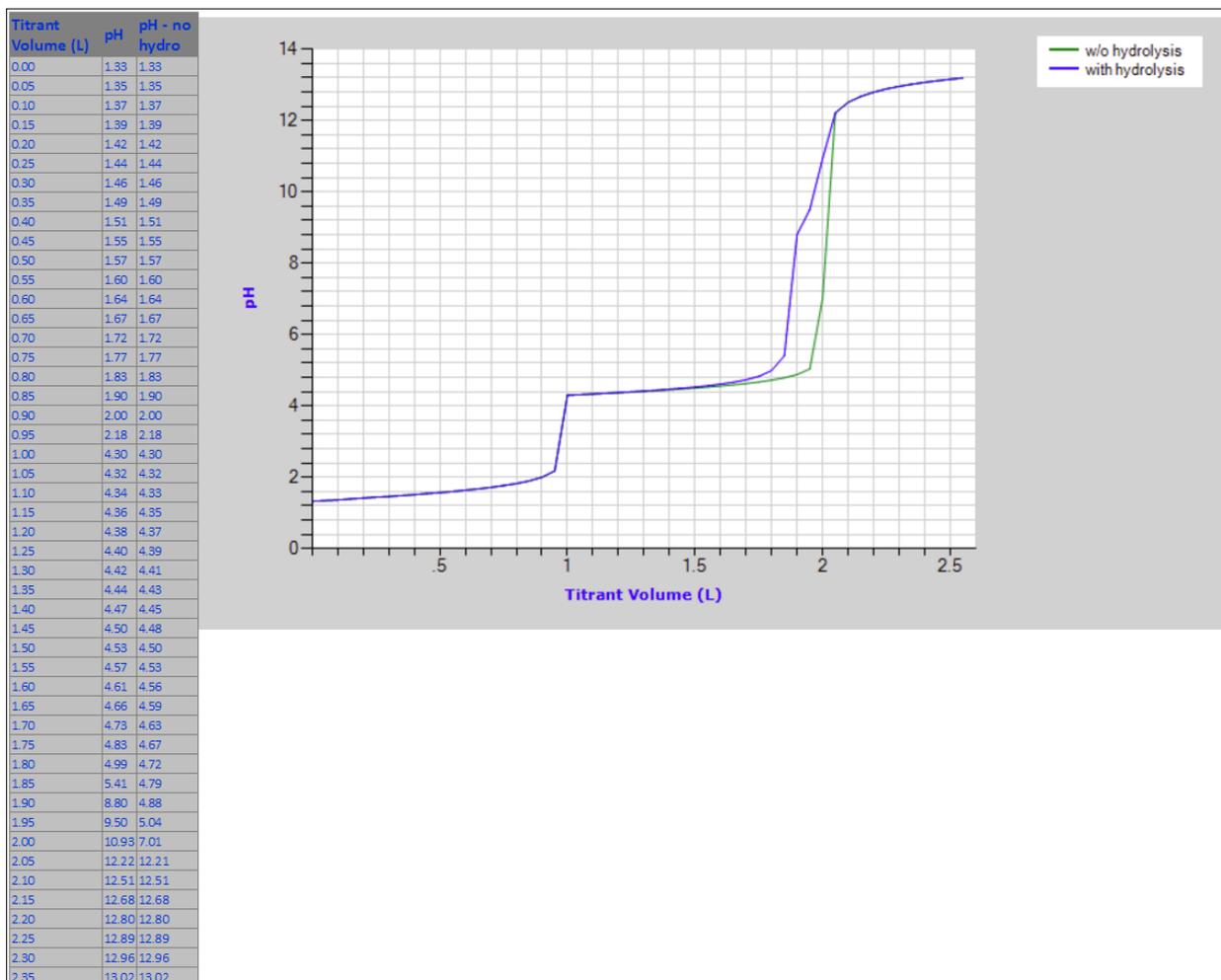
A clear example of hydrolysis can be seen in the following titration, which also demonstrates a second ionization in a polyprotic acid as titrand.

Select Reactants	Species	Type	Initial Volume (L)	Total Amount Added (L)	Concentration (moles/L)	Equilibrium Constant, K
Analyte/Titrant	H ₂ SeO ₃	Weak Acid	1		1	0.0024; 4.8E-09
Reagent/Titrant	NaOH	Strong Base		2.5	1	100000

Reactions:

Titrant 1 st ionization:	H ₂ SeO ₃ [aq]	+	<-->	H(+) [aq]	+	HSeO ₃ (-) [aq]
Titrant 2 nd ionization:	HSeO ₃ (-) [aq]	+	<-->	H(+) [aq]	+	SeO ₃ (-2) [aq]
Titrant ionization:	NaOH [aq]	+	<-->	Na(+) [aq]	+	OH(-) [aq]
Water autoionization:	H ₂ O [liquid]	+	<-->	H(+) [aq]	+	OH(-) [aq]
Hydrolysis:	H ₂ O [liquid]	+	<-->	H ₂ SeO ₃ [aq]	+	OH(-) [aq]
Hydrolysis:	H ₂ O [liquid]	+	<-->	HSeO ₃ (-) [aq]	+	OH(-) [aq]

The simulated results are provided with and without hydrolysis, in order to show the impact of hydrolysis. The first ionization is neutralized when the titrant volume is about 1L and the second ionization is neutralized just before the titrant volume reaches 2L. Hydrolysis significantly speeds up the neutralization of the acid in this particular case and accelerates the pH change – when the titrant volume is just under 2L, hydrolysis increases the pH by more than 4 points.



Conclusion

We have shown how a virtual lab built around ChemReaX can be used to simulate titrations in multiple ways to show the underlying behaviors of the acid-base interactions. Simulations allow various parameters of the reaction to be varied easily, allowing for virtual experimentation. Some of the variables that can be studied include:

- Choice of titrands and titrants – including monoprotic or polyprotic titrands (for acid titrands)
- Variations in titrand and titrant concentrations
- Variations in titrand and titrant volumes
- Effect of hydrolysis on the equivalence point and pH change.

Virtual experiments using simulation allow connections to be made easily between theory and practice, and can significantly enhance the teaching and learning of chemistry.

References

ChemReaX - a chemical reaction modeling and simulation app from ScienceBySimulation – Acid-Base Titrations. Retrieved from <https://www.sciencebysimulation.com/chemreax/AnalyzerAB.aspx>

Dill, D. (2008). Notes on General Chemistry. Department of Chemistry, Boston University. Retrieved from <http://www.bu.edu/quantum/notes/GeneralChemistry/index.html>