

Chapter 11

Acid – Base Titrations

It's not over yet. Apply all we know about acid/base chemistry to construct titration curves. (Graphs of pH (y-axis) vs. mL titrant (x-axis))

From titration curves can:

1. Determine analyte concentration
2. Determine acid K_a (base K_b)

By Chapter 11 section:

- 1) Strong acid/strong base titration curve
- 2) Weak acid/strong base titration curve
- 3) Weak base/strong acid titration curve
- 4) Diprotic titration curves
- 5) Potentiometric titrations (Lab)
- 6) Endpoints using visible indicators
- 7) Practical notes (Labs)
- 8) Leveling (Skip)
- 9) Spreadsheets (Skip)

Start with Section 1 – the simplest because the titration curve is just a glorified stoichiometry problem for strong acid/base titrations.

The 1st step always, regardless of the type of titration curve, is to write the balance reaction

Titrate 100 mL of 0.100 M HCl with 0.100 M NaOH

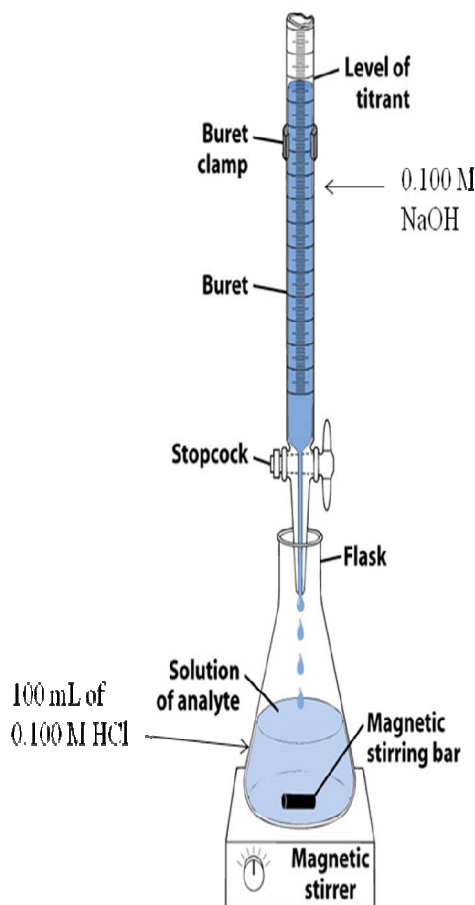


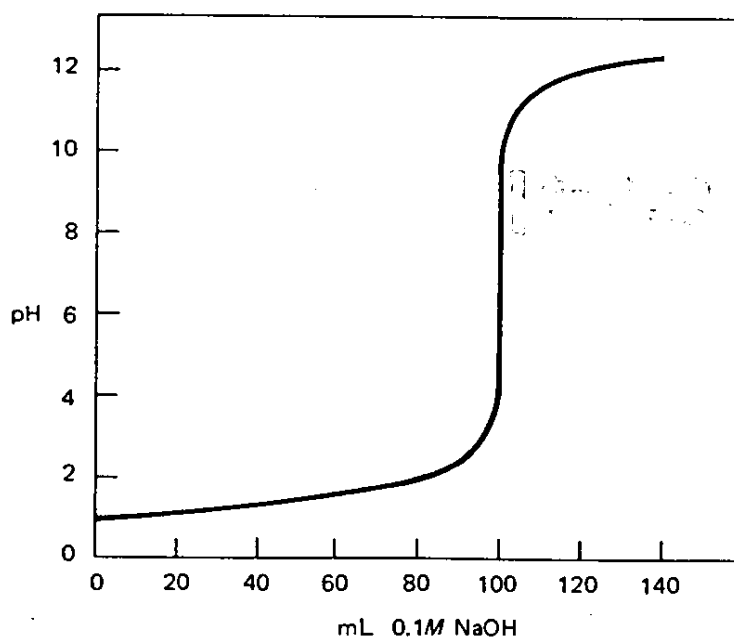
Figure 7-1
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There are 3 regions, or 3 different types of calculations, in a strong acid/strong base titration curve:

- A. Before the equivalence point – in this example not all H^+ is reacted. Calculate $[\text{H}^+]$ and then pH.
- B. At the equivalence point – for this example all H^+ reacted by a stoichiometric amount of OH^-
- C. Past the equivalence point – for this example more OH^- added than H^+ present from HCl. Calculate $[\text{OH}^-]$ added in excess.

If the titration were backwards, that is titrate 100 mL of NaOH with 0.100 M HCl, go through the same reasoning.

Since everything depends on where you are relative to the equivalence point, it is most useful (for all titration curves not just strong acid/base) to know the volume of titrant required to get to the equivalence point.



2 calculations before the equivalence point:

1. Calculate pH before titration begins.
2. Calculate pH after adding 90 mL NaOH.
Calculate $[H^+]$ which is as yet unreacted.

At the equivalence point, that is after adding 100 mL NaOH:

Past the equivalence point, after adding 110 mL of NaOH, calculate the $[OH^-]$ unreacted with H^+ , that is added in excess.

Section 2 – Weak acid/strong base titration curve.

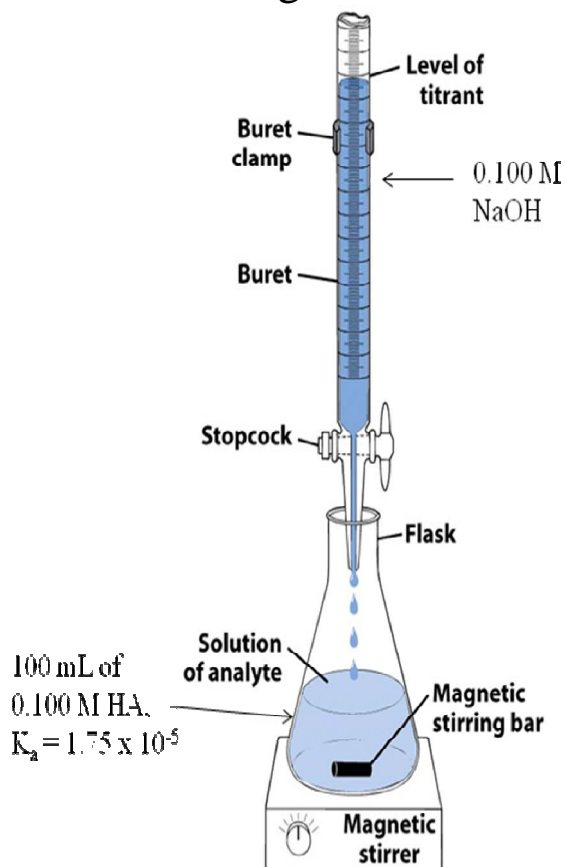


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Remember the 1st step is to write the equation for the titration reaction.

For this type of titration there are 4 regions, that is, 4 different calculations depending on where you are in the titration. In each region you may ask yourself – how did I get here? No don't. Ask yourself what in the solution will dictate the solution pH.

Region 1: Before base is added, a weak acid solution.

Region 2: After base is added but before equivalence point, a mixture of a weak acid and its conjugate base.

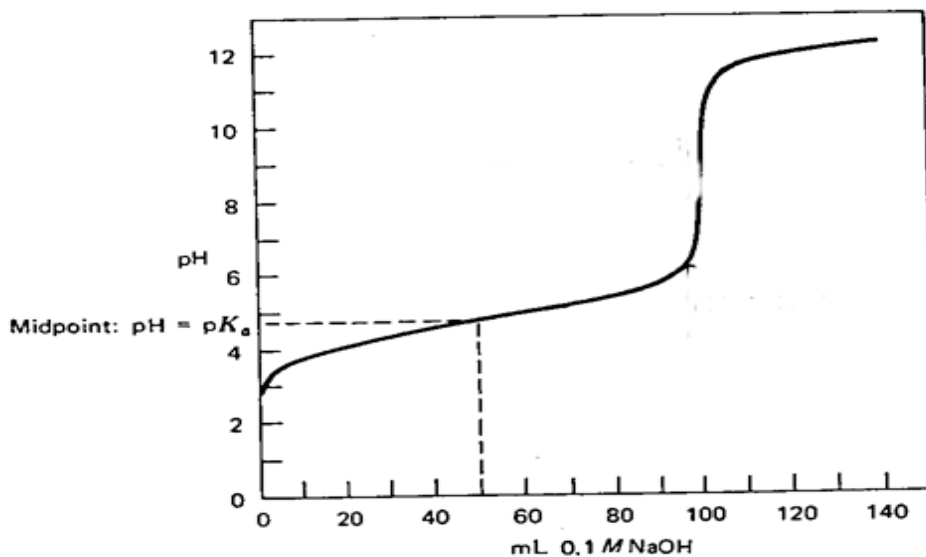
Region 3: At equivalence point, a weak base solution (conjugate to acid).

Region 4: Past equivalence point – pH determined by strong base concentration.

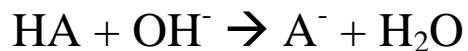
As always everything depends on where you are relative to the equivalence point. So the 2nd step in these titration calculations is to calculate the volume of titrant to reach the equivalence point.

Now that you can orient yourself with respect to the equivalence point, you are in a position to determine what exists in the solution that determines the pH.

Region 1: before base is added – HA in water = weak acid problem.



Region 2 – After base is added but before equivalence point.



Some (not all) HA has been converted to A^- .

HA/ A^- mixture.

Ex. After 30 mL of NaOH titrant is added:

Region 3 – At equivalence point. 10 mmol OH^- (100 mL is added. So All HA has been reacted to form its conjugate base A^- , a weak base.

Region 4 – Past equivalence point. Excess NaOH added beyond the mmol of HA analyte.
Ex. 10 mL (1 mmol excess) OH⁻.

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Section 11-3. Weak Base Strong Acid titration

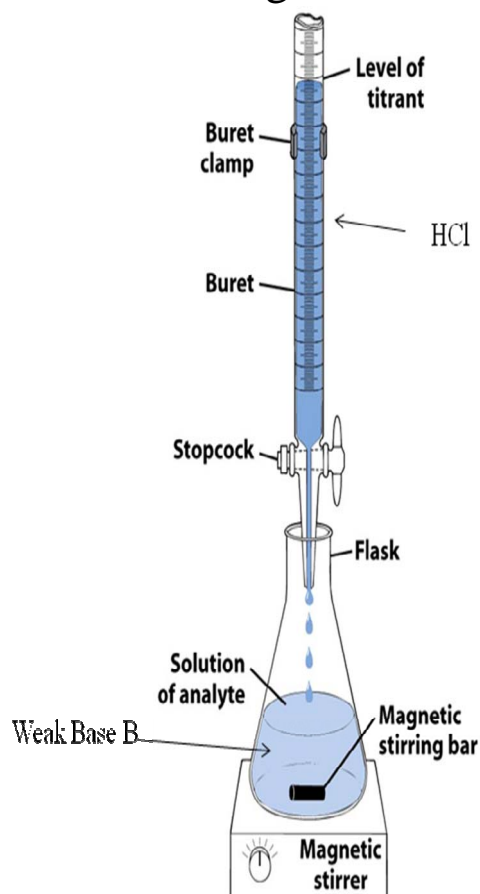
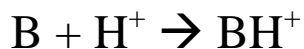


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Only a discussion in general because it is the same thought process as the weak acid/strong base titration, just in reverse.

First order of business: the titration reaction.



Region 1 - before acid titrant (HCl) is added. The solution contains only B.

Region 2 – after some strong acid is added but before the equivalence point, a mixture of base and conjugate acid B/BH⁺.

Region 3 – at equivalence point, all of the weak base has been reacted to form its conjugate acid.

Region 4 – past equivalence point the pH is dictated by the concentration of extra strong acid added that is unreacted by analyte B.

Review sections 1 – 3.

Section 1 – Strong Acid/Strong Base. Just stoichiometry, no equilibria. Trick is to remember dilution.

Section 2 – Weak Acid/Strong Base Titration (Always assumed that the strong acid or base is the titrant).

1. Before adding base: A weak acid problem.
2. After adding some base but before equivalence point: A buffer problem.
3. At equivalence point: Weak base problem.
4. Past equivalence point: Strong base problem.

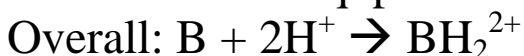
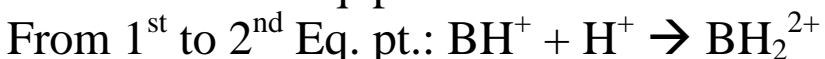
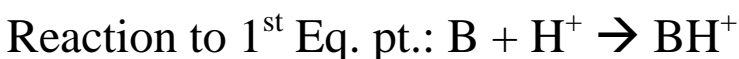
Section 3 – Weak Base/Strong Acid titration

1. Before adding acid: A weak base problem.
2. After adding acid but before equivalence point: A buffer problem.
3. At equivalence point: A weak acid problem.
4. Past equivalence point: Strong acid problem.

Region	Weak A/Strong B	Weak B/Strong A
1 – before start	Weak Acid	Weak Base
2 – before E.P.	Buffer	Buffer
3 – at E.P.	Weak Base	Weak Acid
4 – past E.P.	Strong Base	Strong Acid

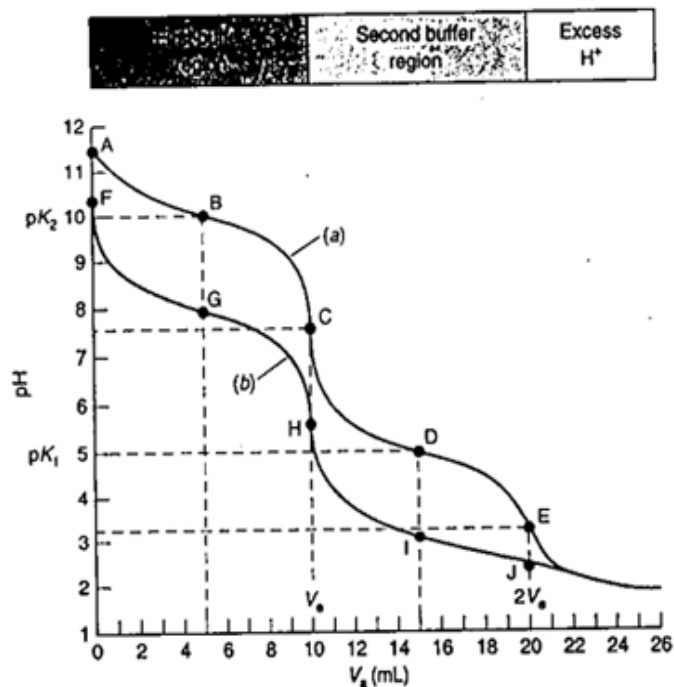
Section 11-4 Diprotic systems

Titrate 10.00 mL of 0.1000 M base (B) with 0.1000 M HCl.
The weak base has $pK_{b1} = 4$, $pK_{b2} = 9$.



First things first: titrant volume to 1st and 2nd Equivalence points.

Figure 12-4 (a) Titration of 10.0 mL of 0.100 M base ($pK_{b1} = 4.00$, $pK_{b2} = 9.00$) with 0.100 M HCl. The two equivalence points are C and E. Points B and D are the half-neutralization points, whose pH values equal pK_{a2} and pK_{a1} , respectively. (b) Titration of 10.0 mL of 0.100 M nicotine ($pK_{b1} = 6.15$, $pK_{b2} = 10.85$) with 0.100 M HCl. There is no sharp break at the second equivalence point, J, because the pH is too low.



Point A – before titration begins. Recall in Chapter for a diprotic (or dibasic) compound the pH governed by K_{b1} .

Point B – Halfway to 1st equivalence point (0.5 mmol H^+ added). First buffer region.

Point C – At 1st equivalence point, amphiprotic BH^+ in solution.

Point D – halfway between 1st and 2nd equivalence points, 2nd buffer region.

Point E – 2nd equivalence point, BH_2^{2+} in solution. Recall from Chapter 10 that the pH from a fully protonated form of a multiprotic acid is governed by K_{a1} .

After the 2nd equivalence point the pH is determined by $[\text{H}^+]$ in excess, as before.

Note: in potentiometric titration lab, we have the opposite situation, that of a weak diprotic acid titrated with a strong base.

Section 11-5 is covered in that potentiometric titration lab referred to above.

Section 11-6 Acid/Base indicators

The goal is for an indicator to change color at the equivalence point pH.

This occurs when 2 requirements are met:

1. If the acid/base indicator compound's conjugate forms exhibit different colors, and
2. The pK_a of the indicator is as close as possible to the equivalence point pH.

A weak acid is given as HA.

A weak acid indicator is given as HIn.

Section 11-7 practical notes such as primary standards, CO_2 , etc. This is applicable to lab and lab final, not lecture. Sections 11-8, 11-9 will be skipped.

Chapter 11 Exercises A – D, F

Problems 1, 2, 4, 6, 8, 12-15, 17-19, 23, 24, 36-38, 40-43, 45.