

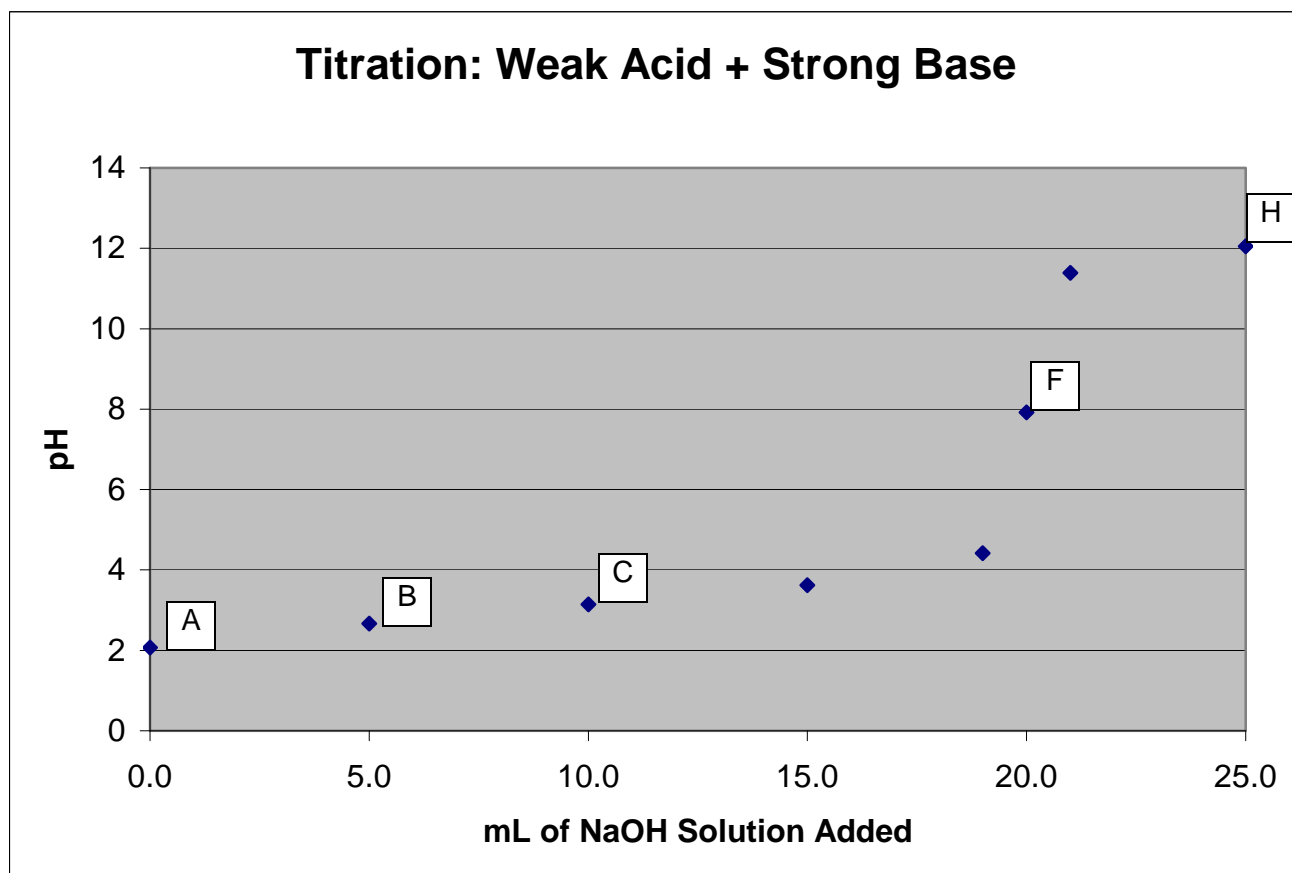
Titration Examples; Zumdahl 7e, section 15.4

Weak Acid + Strong Base EXAMPLE

weak acid: 20.0 mL of 0.100 M hydrofluoric acid, HF ($K_a=7.2 \times 10^{-4}$; $pK_a=3.14$)
titrated with: 0.100 M NaOH

Data:

point	Total Volume of NaOH solution added (mL)	pH
A	0.0	2.07
B	5.0	2.67
C	10.0	3.14
D	15.0	3.62
E	19.0	4.42
F	20.0	7.92
G	21.0	11.39
H	25.0	12.05



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Point A: (20.0 mL of 0.100 M HF + 0.0 mL of 0.100 M NaOH)

What is controlling the pH at this point? (What is the equilibrium reaction at this point?)

Point B: (20.0 mL of 0.100 M HF + 5.0 mL of 0.100 M NaOH)

Calculate the number of moles (or millimoles) for the following reaction *that goes to completion*:

	HF	+	OH ⁻	→	F ⁻	+	H ₂ O
before=					<u>0.0 mmol</u>		---
react.=	- _____		- _____		+ _____		---
complete=	_____ <u>mmol</u>		<u>0.0 mmol</u>		_____ <u>mmol</u>		---

After the complete reaction of the weak acid (HF) with the strong base (NaOH or simply OH⁻), what major species remain in the solution?

What is "special" about a mixture of these two species?

How could you easily find the pH of this solution?

Calculate the pH of the solution at point B:

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Point C: (20.0 mL of 0.100 M HF + 10.0 mL of 0.100 M NaOH)

Calculate the number of moles (or millimoles) for the following reaction *that goes to completion*:

	HF	+	OH ⁻	→	F ⁻	+	H ₂ O
before=					<u>0.0 mmol</u>		---
react.=	- _____		- _____		+ _____		---
complete=	_____ <u>mmol</u>		<u>0.0 mmol</u>		_____ <u>mmol</u>		---

After the complete reaction of the weak acid (HF) with the strong base (NaOH or simply OH⁻), what major species remain in the solution?

Point C in this titration is called the *1/2-way point*. Why is it called this?

Calculate the pH of the solution at point C:

What is unusual about the pH at the 1/2-way point?

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Point F: (20.0 mL of 0.100 M HF + 20.0 mL of 0.100 M NaOH)

Calculate the number of moles (or millimoles) for the following reaction *that goes to completion*:

	HF	+	OH ⁻	→	F ⁻	+	H ₂ O
before=					<u>0.0 mmol</u>		---
react.=	- _____		- _____		+ _____		---
complete=	_____ <u>mmol</u>		<u>0.0 mmol</u>		_____ <u>mmol</u>		---

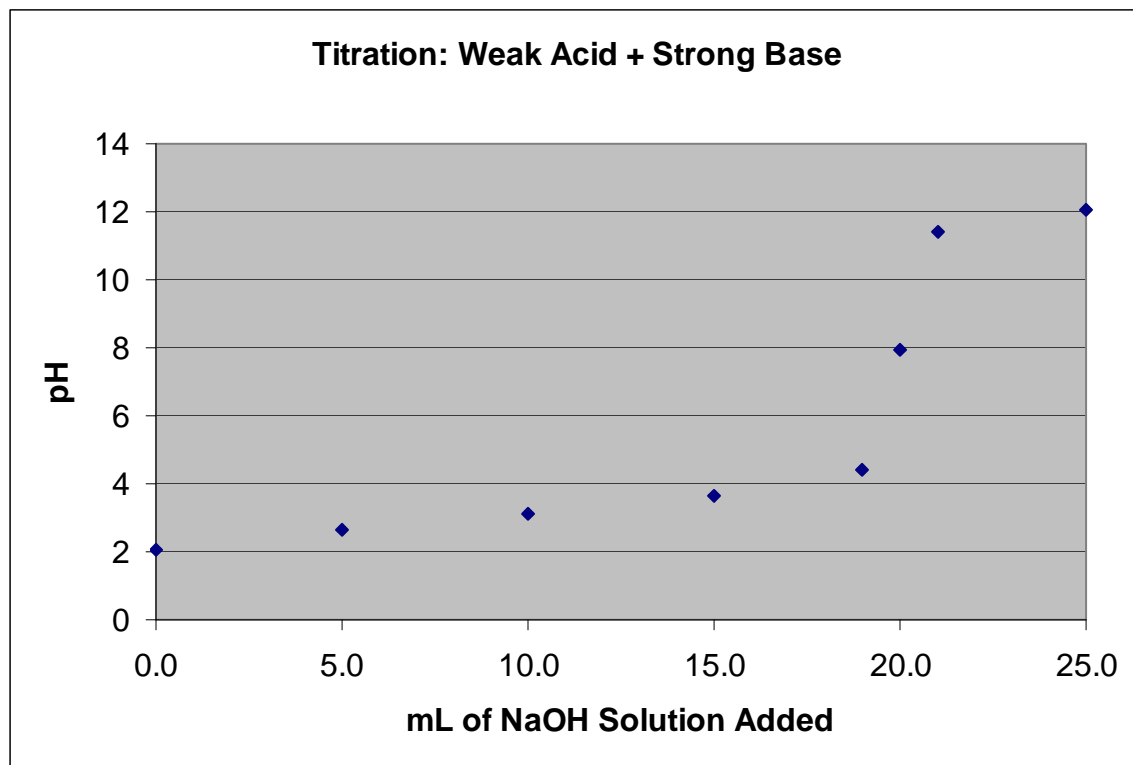
After the complete reaction of the weak acid (HF) with the strong base (NaOH or simply OH⁻), what major specie(s) remain(s) in the solution?

What is controlling the pH at this point? (What is the equilibrium reaction at this point?)

Point F in this titration is called the *equivalence point*. Why is it called this?

What is the concentration of fluoride $[F^-]$ at this point?

Calculate the pOH, and then pH, at the equivalence point. (ref.: for HF, $K_a = 7.2 \times 10^{-4}$ and for a conjugate acid/base pair: $K_a \times K_b = K_w = 1.00 \times 10^{-14}$)



Some Conclusions Thus Far:

- I. At some point, before any (strong base) has been added, the pH is controlled by the equilibrium of the weak acid; **note this point on the graph above**. The equilibrium is $\text{HF} \leftrightarrow \text{H}^+ + \text{F}^-$ ($K_a = 7.2 \times 10^{-4}$ or $\text{p}K_a = 3.14$) in this example. We calculate pH by setting up an initial/reaction/equilibrium table and setting this equal to K_a .
- II. After we start to add the titrant (OH^- , in this example), but before the equivalence point, we have a buffer; **note the buffer region on the graph above**. The pH is controlled by the relative quantities (concentrations) of acid and conjugate base, and is easily calculated using the Henderson-Hasselbalch equation. (*I think that some have jokingly called this the David-Hasselhoff equation, but that seems a little irreverent to me.*)
- III. At the $\frac{1}{2}$ -way point (point C in this example), the $\text{pH} = \underline{\hspace{2cm}}$. (**Answer this question, and note the $\frac{1}{2}$ -way point on the graph above.**)
- IV. What happens to the pH as the titration nears the equivalence point? (**Answer this question and note the equivalence point on the graph above.**)

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Point H: (20.0 mL of 0.100 M HF + 25.0 mL of 0.100 M NaOH)

Calculate the number of moles (or millimoles) for the following reaction *that goes to completion*:

	HF	+	OH ⁻	→	F ⁻	+	H ₂ O
before=					<u>0.0 mmol</u>		---
react.=	- _____		- _____		+ _____		---
complete=	<u>0.0 mmol</u>		_____ mmol		_____ mmol		---

After the complete reaction of the weak acid (HF) with the strong base (NaOH or simply OH⁻), what major species remain in the solution?

What is controlling the pH at this point? (What is the strongest base remaining in solution?)

Calculate the pH at this point.

More Conclusions:

V. *After* the equivalence point, how much of the weak acid remains?

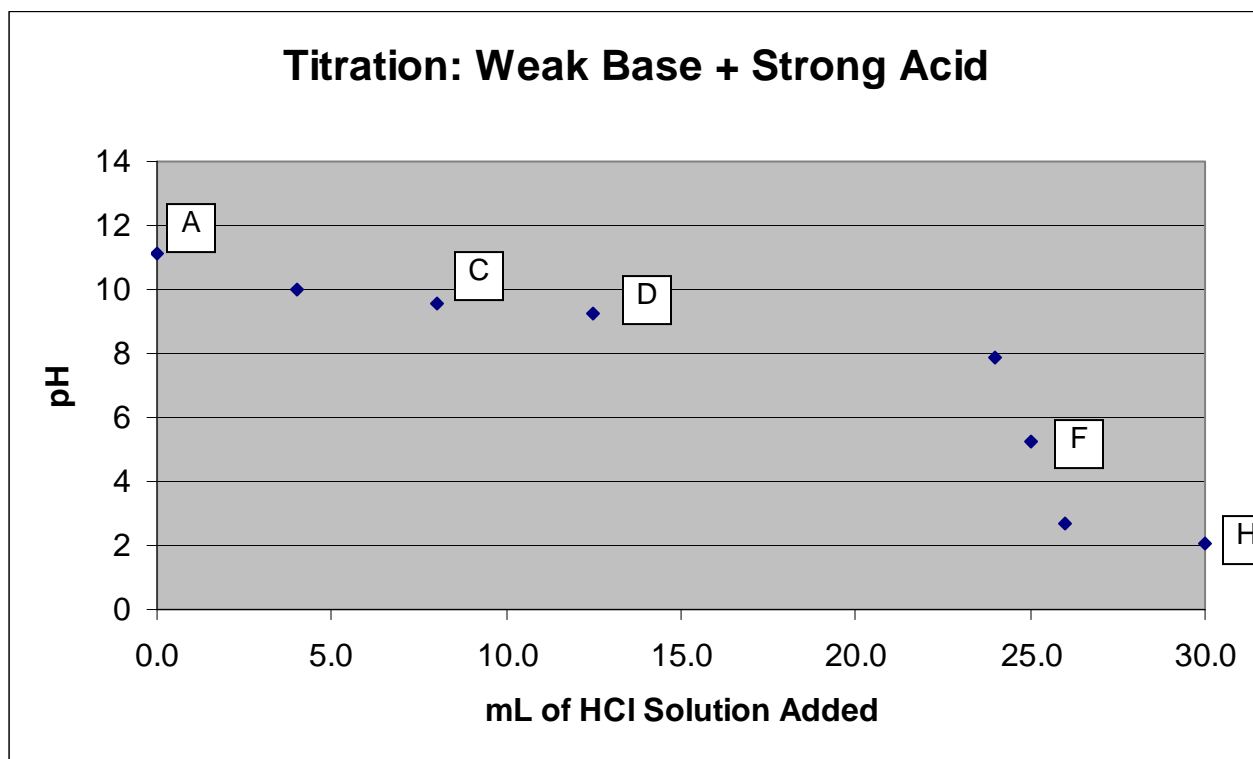
Do we still have a buffer? How did you calculate the pH in this region?

Weak Base + Strong Acid EXAMPLE

weak base: 25.0 mL of 0.100 M aqueous ammonia, NH_3 ($K_b = 1.8 \times 10^{-5}$)
titrated with: 0.100 M HCl

Data:

point	Total Volume of HCl solution added (mL)	pH
A	0.0	11.13
B	4.0	9.97
C	8.0	9.58
D	12.5	9.25
E	24.0	7.87
F	25.0	5.28
G	26.0	2.71
H	30.0	2.04



On the graph on page 8, identify:

1. point at which pH is controlled by NH_3 concentration only
2. buffer region
3. $\frac{1}{2}$ -way point
4. equivalence point
5. point at which pH is controlled by NH_4^+ concentration only
6. region at which pH is controlled by HCl concentration only

The math involved in the titration of a weak base + a strong acid is exactly the same as weak acid + strong base, however, as we would expect, the pH values are "flipped".

For a Weak Base + Strong Acid titration:

Before any strong acid has been added, the pH is controlled by the equilibrium of the weak base. The equilibrium is $\text{NH}_3 + \text{H}_2\text{O} \leftrightarrow \text{OH}^- + \text{NH}_4^+$ ($K_b = 1.8 \times 10^{-5}$) in this example. We calculate pH by setting up an initial/reaction/equilibrium table and setting this equal to K_b .

After we start to add the titrant (HCl or H^+ , in this example), but before the equivalence point, we have a buffer. The pH is controlled by the relative quantities (concentrations) of weak base and its conjugate acid, and is easily calculated using the Henderson-Hasselbalch equation (using K_a for the conjugate acid). **At the $\frac{1}{2}$ -way point**, the $\text{pH} = \text{p}K_a$ (for the conjugate acid).

What happens to the pH as the titration nears the equivalence point?

At the equivalence point, all of the weak base (NH_3) has been converted to its conjugate acid (NH_4^+). The pH is controlled by the equilibrium of the (weak) conjugate acid. We calculate pH by setting up an initial/reaction/equilibrium table and setting this equal to K_a .

After the equivalence point, all of the weak base is "used up". The pH is controlled by the strongest acid in solution, which is the strong acid that is being added. The pH is simply calculated as if the solution only contains a strong acid (HCl in this example).

Calculate K_a and $\text{p}K_a$ for the conjugate acid (NH_4^+) of the weak base used in this example. (recall that for a conjugate acid/base pair: $K_a \times K_b = K_w = 1.00 \times 10^{-14}$)

At the $\frac{1}{2}$ -way point (point D in this example), the $\text{pH} = \dots$

Point A: 25.0 mL of 0.100 M aqueous ammonia, NH_3 + 0.0 mL of 0.100 M HCl

What is controlling the pH at this point? (What is the equilibrium reaction at this point?)

Calculate the pH at point A: ($K_b = 1.8 \times 10^{-5}$)

Point C: 25.0 mL of 0.100 M aqueous ammonia, NH_3 + 8.0 mL of 0.100 M HCl

What is the reaction that goes to completion at this point?

What are the major species in solution at this point? What are the quantities (mmol) of each of these ions or molecules?

Calculate the pH at point C:

Point D: 25.0 mL of 0.100 *M* aqueous ammonia, NH_3 + 12.5 mL of 0.100 *M* HCl

What is the reaction that goes to completion at this point?

What are the major species in solution at this point? What are the quantities of each?

Calculate the pH at point D:

Point F: 25.0 mL of 0.100 *M* aqueous ammonia, NH_3 + 25.0 mL of 0.100 *M* HCl

What is the reaction that goes to completion at this point?

What are the major species in solution at this point? What are the quantities of each?

Calculate the pH at point F:

Point H: 25.0 mL of 0.100 *M* aqueous ammonia, NH_3 + 30.0 mL of 0.100 *M* HCl

What is the reaction that goes to completion at this point?

What are the major species in solution at this point? What are the quantities of each? Which is the strongest acid remaining in solution?

Calculate the pH at point H: