Content Background and Information—Acid-Base, Titrations

As you go through the acid–base equilibrium unit, keep a running list on the board, differentiating how you solve for pH of all the different types of solutions that we can get. Recall:

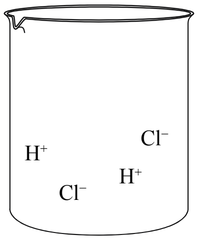
Strong Acid → $pH = -\log[\text{acid}]$
Weak Acid → (ICE) $K_a = \dfrac{x^2}{\text{initial} - x}$: $x = [H^+]$; $pH = -\log[H^+]$
Strong Base → $pOH = -\log[\text{base}]$: $pH = 14 - pOH$
Weak Base → (ICE) $K_b = \dfrac{x^2}{\text{initial} - x}$; $x = [OH^-]$; $pOH = -\log[OH^-]$; $pH = 14 - pOH$
Salts: Identify ionic compound; any ion that is conjugate of a strong acid/base does nothing; any ion that is a conjugate of a weak acid/base behaves as the conjugate would Acidic→ refer to weak acid Basic → refer to weak base Neutral → no effect on pH (pH = 7 if salt is only species present)
Buffer → $[H^+] = K_a \dfrac{[\text{acid}]}{[\text{base}]}$; $pH = -\log[H^+]$ (or use Henderson-Hasselbach if you prefer)
Buffer invaded → $[H^+] = K_a \dfrac{[\text{weak acid} \pm \text{invader moles}]}{[\text{weak base} \pm \text{invader moles}]}$; $pH = -\log[H^+]$ ** If the buffer is invaded by a base, add to the base, subtract from the acid ** If the buffer is invaded by an acid, add to the acid, subtract from the base.

As you progress through the unit, work on recognizing, and calculating pH with each of these. Then you get to titrations where you put it all together.

Focus heavily on "What's in the beaker?", trying to identify one of these six options.

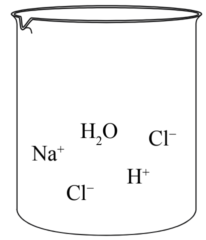
Start out with simple drawings, first involving a strong acid being titrated with a strong base. The beakers will show what is in the beaker as 0, 1, 2 and 3 moles of NaOH are added to 2 moles of HCl.

Beaker 1: 2 moles HCl + 0 moles NaOH



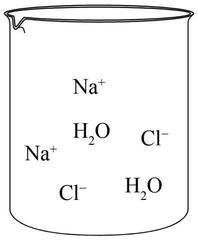
What's in the Beaker?
Strong acid

Beaker 2: 2 moles HCl + 1 mole NaOH



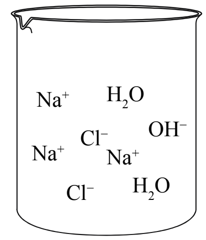
What's in the Beaker?
Strong acid; neutral salt

Beaker 3: 2 moles HCl + 2 moles NaOH



What's in the Beaker?
Neutral salt

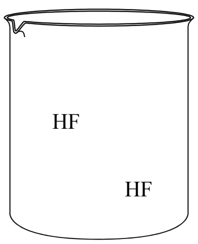
Beaker 4: 2 moles HCl + 3 moles NaOH



What's in the Beaker?
Neutral salt; strong base

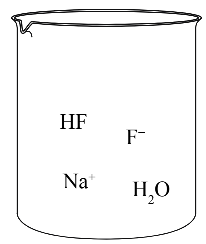
Then move to a weak acid titrated with a strong base. The beakers will show what is in the beaker as 0, 1, 2 and 3 moles of NaOH are added to 2 moles of HF.

Beaker 1: 2 moles HF + 0 moles NaOH



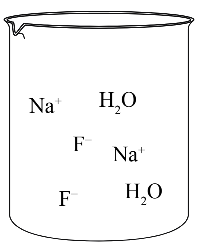
What's in the Beaker?
Weak acid

Beaker 2: 2 moles HF + 1 mole NaOH



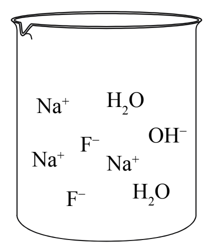
What's in the Beaker?
Weak acid; basic salt → BUFFER!

Beaker 3: 2 moles HF + 2 moles NaOH



What's in the Beaker?
Basic salt

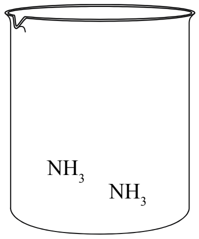
Beaker 4: 2 moles HF + 3 moles NaOH



What's in the Beaker?
Basic salt; strong base

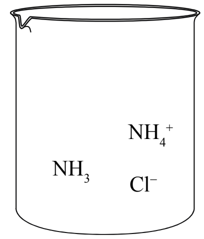
Finally, move to a weak base titrated with a strong acid. The beakers will show what is in the beaker as 0, 1, 2 and 3 moles of HCl are added to 2 moles of NH_3.

Beaker 1: 2 moles NH_3 + 0 moles HCl



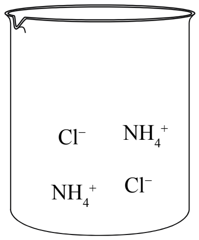
What's in the Beaker?
Weak base

Beaker 2: 2 moles NH_3 + 1 moles HCl



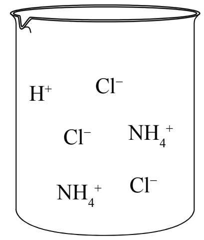
What's in the Beaker?
Weak base; acidic salt → BUFFER!

Beaker 3: 2 moles NH_3 + 0 moles HCl



What's in the Beaker?
Acidic salt

Beaker 4: 2 moles NH_3 + 0 moles HCl

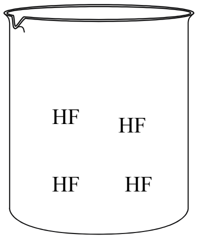


What's in the Beaker?
Acidic salt; strong acid

To highlight the importance of the equivalence point and the idea that there are 4 “zones” in a titration, repeat the weak acid/strong base titration but with a higher amount of initial weak acid.

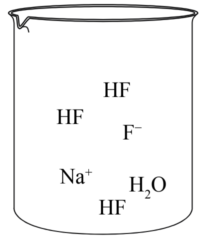
Suppose the titration were of 4 moles of HF with 0 to 6 moles of NaOH. This titration demonstrates that from 0 to equivalence creates a buffer. In addition, it also demonstrates the ½ equivalence point.

Beaker 1: 4 moles HF + 0 moles NaOH



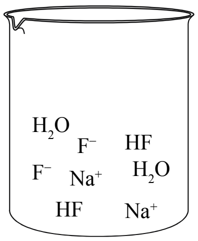
What’s in the Beaker?
Weak acid

Beaker 2: 4 moles HF + 1 mole NaOH



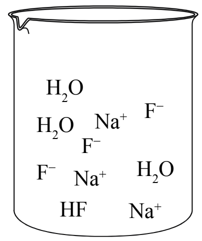
What’s in the Beaker?
Weak acid; basic salt → BUFFER!

Beaker 3: 4 moles HF + 2 moles NaOH



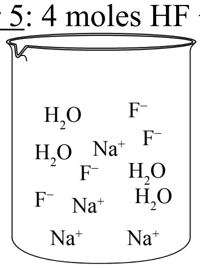
What’s in the Beaker?
Weak acid; basic salt→ BUFFER!

Beaker 4: 4 moles HF + 3 moles NaOH



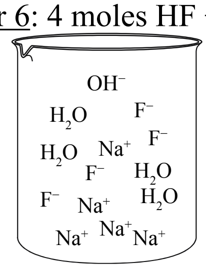
What’s in the Beaker?
Weak acid; basic salt→ BUFFER!

<u>Beaker 5</u>: 4 moles HF + 4 moles NaOH



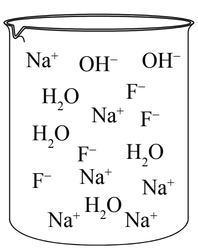
What’s in the Beaker?
Basic salt

<u>Beaker 6</u>: 4 moles HF + 5 moles NaOH



What’s in the Beaker?
Basic salt; strong base

<u>Beaker 7</u>: 4 moles HF + 6 moles NaOH



What’s in the Beaker?
Basic salt; strong base

There are 4 points of interest along a titration curve for weak acids/bases with strong bases/acids.

1. The pH before the titration begins. Only the weak acid or the weak base is present. The pH is determined through an ICE diagram with K_a or K_b as appropriate.
2. The pH between the beginning and the equivalence point. A buffer solution is present in this portion. Note: halfway to the equivalence point, pH = pK_a. The buffer equation can be used anywhere along this portion.
3. The pH at the equivalence point. Since the moles of acid/base originally present equal the moles of base/acid added, neither species remains in the solution. All that is present is the salt and water. Find the pH of the salt through a hydrolysis reaction with an ICE diagram.
4. The pH past the equivalence point. There is excess of the strong acid or base. The strong substance dictates the pH as it splits up completely. The pH can be determined using the number of moles of excess strong divided by the total volume of the solution in liters.

EXAMPLES

1. Calculate the pH at the given points in the titration between 30.00 mL of 0.2000 M HCl and the given volumes of 0.2000 M NaOH. ** There are 6 mmol HCl in the beaker to start with.

a. Before any NaOH is added. (0 moles NaOH)

What's in the Beaker? Strong Acid

pH = –log (0.2000) = 0.6990

b. After 10.00 mL of NaOH is added.

There have been (10 mL × 0.2 M=) 2 mmol NaOH added to the flask.

	HCl	NaOH	→	NaCl	H_2O
Initially	6 mmol	2 mmol		0	
After Reaction	4 mmol	0 mmol		2 mmol	

What's in the Beaker? Strong acid, neutral salt

$$[\text{acid}] = \frac{4\text{ mmol}}{40\text{ mL}} = 0.1000\text{ M}$$
$$\text{pH} = -\log(0.1000) = 1.0000$$

c. After 30.00 mL of NaOH is added.

There have been (30 mL × 0.2 M=) 6 mmol NaOH added to the flask.

	HCl	NaOH	→	NaCl	H_2O
Initially	6 mmol	6 mmol		0	
After Reaction	0 mmol	0 mmol		6 mmol	

What's in the Beaker? Neutral salt

pH = 7.0000

d. After 35.00 mL of NaOH is added.

There have been (35 mL × 0.2 M=) 7 mmol NaOH added to the flask.

	HCl	NaOH	→	NaCl	H_2O
Initially	6 mmol	7 mmol		0	
After Reaction	0 mmol	1 mmol		6 mmol	

What's in the Beaker? Strong base, neutral salt

$$[\text{base}] = \frac{1\text{ mmol}}{65\text{ mL}} = 0.01538\text{ M}$$

$$\text{pOH} = -\log(0.01538) = 1.8129$$

$$\text{pH} = 14 - 1.8129 = 12.1871$$

e. After 70.00 mL of NaOH is added.

	HCl	NaOH	→	NaCl	H_2O
Initially	6 mmol	14 mmol		0	
After Reaction	0 mmol	8 mmol		6 mmol	

What's in the Beaker? Strong base, neutral salt

$$[\text{base}] = \frac{8\text{ mmol}}{100\text{ mL}} = 0.08000\text{ M}$$

$$\text{pOH} = -\log(0.08000) = 1.0969$$

$$\text{pH} = 14 - 1.0969 = 12.9031$$

2. Calculate the pH at the given points in the titration between 40.00 mL of 0.1000 M propanoic acid (HPr; $K_a = 1.3\times10^{-5}$) and the given volumes of 0.1000 M NaOH. **Note: There are 4 mmol HPr in the flask to start.

a. 0.00 mL NaOH

What's in the Beaker? Weak Acid

$$1.3\times10^{-5} = \frac{x^2}{0.1000 - x} \quad \text{(assume } 0.1000 - x \sim 0.1000\text{)}$$

$$1.3\times10^{-5} = \frac{x^2}{0.1000}$$

$$x = [\mathrm{H}^+] = 1.140\times10^{-3}$$

$$\mathrm{pH} = -\log(1.140\times10^{-3}) = 2.9431$$

b. 30.00 mL NaOH

There have been (30 mL × 0.1 M=) 3 mmol NaOH added to the flask.

	HPr	NaOH	→	NaPr	H_2O
Initially	4 mmol	3 mmol		0	
After Reaction	1 mmol	0 mmol		3 mmol	

What's in the Beaker? Weak acid, basic salt → Buffer!!

$$[\mathrm{H}^+] = 1.3\times10^{-5} \times \frac{\frac{1\ \text{mmol}}{70\ \text{mL}}}{\frac{3\ \text{mmol}}{70\ \text{mL}}} = 4.333\times10^{-6}$$

$$\mathrm{pH} = -\log(4.333\times10^{-6}) = 5.3631$$

c. 40.00 mL NaOH

There have been (40 mL × 0.1 M=) 4 mmol NaOH added to the flask.

	HPr	NaOH	→	NaPr	H_2O
Initially	4 mmol	4 mmol		0	
After Reaction	0 mmol	0 mmol		4 mmol	

What's in the Beaker? Basic salt

$$K_b = \frac{1\times10^{-14}}{1.3\times10^{-5}} = 7.692\times10^{-10}$$

$$[\text{basic salt}] = \frac{4\text{ mmol}}{80\text{ mL}} = 0.05000\text{M}$$

$$7.692\times10^{-10} = \frac{x^2}{0.05000 - x} \qquad (\text{assume } 0.05000 - x \sim 0.05000)$$

$$7.692\times10^{-10} = \frac{x^2}{0.05000}$$

$$x = [\text{OH}^-] = 6.202\times10^{-6}$$

$$\text{pOH} = -\log(6.202\times10^{-6}) = 5.2075$$

$$\text{pH} = 14 - 5.2075 = 8.7925$$

d. 50.00 mL NaOH

There have been (50 mL × 0.1 M=) 5 mmol NaOH added to the flask.

	HPr	NaOH	→	NaPr	H_2O
Initially	4 mmol	5 mmol		0	
After Reaction	0 mmol	1 mmol		4 mmol	

What's in the Beaker? Strong base, basic salt (basic salt is "over–ridden" by strong base)

$$[\text{base}] = \frac{1\text{ mmol}}{90\text{ mL}} = 0.01111\text{ M}$$

$$\text{pOH} = -\log(0.01111) = 1.9542$$

$$\text{pH} = 14 - 1.9542 = 12.0457$$

3. Calculate the pH at the given points in the titration between 100.0 mL of 0.05000 M NH_3 (Kb = 1.8×10^{-5}) after adding the following volumes of 0.1000 M HCl. Note ** There are 5 mmol NH_3 in the flask to start with.

a. 0.00 mL HCl

What's in the Beaker? Weak Base

$$1.8\times10^{-5} = \frac{x^2}{0.05000 - x} \quad (\text{Assume } 0.05000 - x \sim 0.05000)$$

$$1.8\times10^{-5} = \frac{x^2}{0.05000}$$

$$x = [\text{OH}^-] = 9.487\times10^{-4}$$

$$\text{pOH} = -\log(9.487\times10^{-4}) = 3.0229$$

$$\text{pH} = 14 - 3.0229 = 10.9771$$

b. 10.00 mL HCl

There have been (10 mL × 0.1 M=) 1 mmol HCl added to the flask.

	HCl	NH_3	→	NH_4Cl
Initially	1 mmol	5 mmol		0
After Reaction	0 mmol	4 mmol		1 mmol

What's in the Beaker? Weak base, acidic salt → Buffer!!

$$K_a = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.6\times10^{-10}$$

$$[H^+] = 5.6\times10^{-10} \times \frac{\frac{1\text{ mmol}}{110\text{ mL}}}{\frac{4\text{ mmol}}{110\text{ mL}}} = 1.400\times10^{-10}$$

$$pH = -\log(1.400\times10^{-10}) = 9.8539$$

c. 25.00 mL HCl

There have been (25 mL × 0.1 M=) 2.5 mmol HCl added to the flask.

	HCl	NH_3	→	NH_4Cl
Initially	2.5 mmol	5 mmol		0
After Reaction	0 mmol	2.5 mmol		2.5 mmol

What's in the Beaker? Weak base, acidic salt → Buffer!!

$$[H^+] = 5.6\times10^{-10} \times \frac{\frac{2.5\text{ mmol}}{125\text{ mL}}}{\frac{2.5\text{ mmol}}{125\text{ mL}}} = 5.6\times10^{-10}$$

$$pH = -\log(5.6\times10^{-10}) = 9.2518$$

d. 50.00 mL HCl

There have been (50 mL × 0.1 M=) 5 mmol HCl added to the flask.

	HCl	NH_3	→	NH_4Cl
Initially	5 mmol	5 mmol		0
After Reaction	0 mmol	0 mmol		5 mmol

What's in the Beaker? Acidic salt

$$[\text{weak acid}] = \frac{5\text{ mmol}}{150\text{ mL}} = 0.03333\text{ M}$$

$$5.6\times10^{-10} = \frac{x^2}{0.03333 - x} \qquad (\text{Assume } 0.03333 - x \sim 0.03333)$$

$$5.6\times10^{-10} = \frac{x^2}{0.03333}$$

$$x = [\text{H}^+] = 4.320\times10^{-6}$$

$$\text{pH} = -\log(4.320\times10^{-6}) = 5.3645$$

e. 60.00 mL HCl

There have been (60 mL × 0.1 M=) 6 mmol HCl added to the flask.

	HCl	NH_3	→	NH_4Cl
Initially	6 mmol	5 mmol		0
After Reaction	1 mmol	0 mmol		5 mmol

What's in the Beaker? Strong acid; Acidic salt (strong acid "over–rides" acidic salt)

$$[\text{acid}] = \frac{1\text{ mmol}}{160\text{ mL}} = 6.250\times10^{-3}\text{ M}$$

$$\text{pH} = -\log(6.250\times10^{-3}) = 2.2041$$

Once you have covered the calculations in a titration (making sure to see each of the 6 different types of calculations that they can encounter), give another titration (some weak/strong combination) as a class problem. Break the class up into small groups and ask them to calculate the pH at a particular point in the titration. Then ask them to put up their (x,y) coordinate in the form of (volume of titrant, pH) on a class chart. Have the class self–assess whether each pH makes sense in the context of the titration. The class can accomplish as many pH calculations as you desire, but make sure that at least 1 from each "zone" of the curve are completed (initial, buffer, equivalence, excess strong).

EXERCISE

Hydrogen cyanide gas (HCN), a powerful respiratory inhibitor, is highly toxic. It is a very weak acid ($K_a = 6.2\times10^{-10}$) when dissolved in water. If a 50.0 mL sample of 0.100 M HCN is titrated with 0.100 M NaOH, calculate the pH of the solution when:

a. No NaOH has been added

b. 8.00 mL of NaOH has been added

c. 25.0 mL (total as opposed to additional) of NaOH has been added

d. 50.0 mL (total) of NaOH has been added

e. 100.0 mL (total) of NaOH has been added

SELECTING AN INDICATOR

Choose an indicator with a K_a near that of the acid you are titrating AND whose color changes strongly at the equivalence point.

EXERCISE

Use the table below to determine which indicator would be best to use in the titration of ammonia with hydrochloric acid.

Indicator	**pK_a**
Litmus	6.5
Methyl orange	3.7
Phenolphthalein	9.3

NATIONAL
MATH + SCIENCE
INITIATIVE

This page is intentionally left blank.

www.nms.org