

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<sub>a</sub>. 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  $(10 \text{ mL} \times 0.2 \text{ M}=) 2 \text{ mmol NaOH}$  added to the flask.

	HCI	NaOH	$\rightarrow$	NaCl	H <sub>2</sub> O
Initially	6 mmol	2 mmol		0	
After Reaction	4 mmol	0 mmol		2 mmol	

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

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

c. After 30.00 mL of NaOH is added.

There have been  $(30 \text{ mL} \times 0.2 \text{ M}=) 6 \text{ mmol NaOH}$  added to the flask.

	HCI	NaOH	-	NaCl	H <sub>2</sub> O
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  $\times$  0.2 M=) 7 mmol NaOH added to the flask.

****	HCl	NaOH	<b>→</b>	NaCl	H <sub>2</sub> O
Initially	6 mmol	7 mmol		0	
After Reaction	0 mmol	1 mmol		6 mmol	

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

[base] = 
$$\frac{1 \text{ mmol}}{65 \text{ mL}}$$
 = 0.01538 M  
pOH =  $-\log (0.01538)$  = 1.8129  
pH = 14 -1.8129 = 12.1871

e. After 70.00 mL of NaOH is added.

March 1	HCl	NaOH		NaCl	H <sub>2</sub> O
Initially	6 mmol	14 mmol		0	·
After Reaction	0 mmol	8 mmol		6 mmol	

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

[base] = 
$$\frac{8 \text{ mmol}}{100 \text{ mL}}$$
 = 0.08000 M  
pOH =  $-\log (0.08000)$  = 1.0969  
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;  $K_a = 1.3 \times 10^{-5}$ ) 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

$$1.3 \times 10^{-5} = \frac{x^2}{0.1000 - x} \quad \text{(assume } 0.1000 - x \sim 0.1000)$$

$$1.3 \times 10^{-5} = \frac{x^2}{0.1000}$$

$$x = [H^+] = 1.140 \times 10^{-3}$$

$$pH = -\log(1.140 \times 10^{-3}) = 2.9431$$

b. 30.00 mL NaOH

There have been  $(30 \text{ mL} \times 0.1 \text{ M}=) 3 \text{ mmol NaOH}$  added to the flask.

	HPr	NaOH	$\rightarrow$	NaPr	H <sub>2</sub> O
Initially	4 mmol	3 mmol		0	
After Reaction	1 mmol	0 mmol		3 mmol	

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

$$[H^{+}] = 1.3 \times 10^{-5} \times \frac{\frac{1 \text{ mmol}}{70 \text{ mL}}}{\frac{3 \text{ mmol}}{70 \text{ mL}}} = 4.333 \times 10^{-6}$$

$$pH = -\log(4.333 \times 10^{-6}) = 5.3631$$

c. 40.00 mL NaOH

There have been  $(40 \text{ mL} \times 0.1 \text{ M}=) 4 \text{ mmol NaOH}$  added to the flask.

	HPr	NaOH	 NaPr	H <sub>2</sub> O
Initially	4 mmol	4 mmol	0	
After Reaction	0 mmol	0 mmol	4 mmol	

What's in the Beaker? Basic salt

$$K_b = \frac{1 \times 10^{-14}}{1.3 \times 10^{-5}} = 7.692 \times 10^{-10}$$
[basic salt] =  $\frac{4 \text{ mmol}}{80 \text{ mL}} = 0.05000\text{M}$ 

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

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

$$x = [OH^-] = 6.202 \times 10^{-6}$$

$$pOH = -\log(6.202 \times 10^{-6}) = 5.2075$$

$$pH = 14 - 5.2075 = 8.7925$$

#### d. 50.00 mL NaOH

There have been  $(50 \text{ mL} \times 0.1 \text{ M}=) 5 \text{ mmol NaOH}$  added to the flask.

	HPr	NaOH	$\rightarrow$	NaPr	H <sub>2</sub> O
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)

[base] = 
$$\frac{1 \text{ mmol}}{90 \text{ mL}}$$
 = 0.01111 M  
pOH =  $-\log(0.01111)$  = 1.9542  
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<sub>3</sub> (Kb =  $1.8 \times 10^{-5}$ ) after adding the following volumes of 0.1000 M HCl. Note \*\* There are 5 mmol NH<sub>3</sub> in the flask to start with.
  - a. 0.00 mL HCl

What's in the Beaker? Weak Base

$$1.8 \times 10^{-5} = \frac{x^2}{0.05000 - x}$$
 (Assume 0.05000 -  $x \sim 0.05000$ )  

$$1.8 \times 10^{-5} = \frac{x^2}{0.05000}$$
  

$$x = [OH^-] = 9.487 \times 10^{-4}$$
  

$$pOH = -\log(9.487 \times 10^{-4}) = 3.0229$$
  

$$pH = 14 - 3.0229 = 10.9771$$



### b. 10.00 mL HCl

There have been  $(10 \text{ mL} \times 0.1 \text{ M}=) 1 \text{ mmol HCl}$  added to the flask.

	HCl	NH <sub>3</sub>	-	NH <sub>4</sub> Cl
Initially	1 mmol	5 mmol		0
After Reaction	0 mmol	4 mmol		1 mmol

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

$$K_{_a} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

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

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

## c. 25.00 mL HCl

There have been  $(25 \text{ mL} \times 0.1 \text{ M}=) 2.5 \text{ mmol HCl}$  added to the flask.

	HCI	NH,	<b>→</b>	NH <sub>4</sub> Cl
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!!

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

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

d. 50.00 mL HCl

There have been  $(50 \text{ mL} \times 0.1 \text{ M}=) 5 \text{ mmol HCl}$  added to the flask.

******	HCl	NH <sub>3</sub>	<b>→</b>	NH₄Cl
Initially	5 mmol	5 mmol		0
After Reaction	0 mmol	0 mmol		5 mmol

What's in the Beaker? Acidic salt

[weak acid] = 
$$\frac{5 \text{ mmol}}{150 \text{ mL}} = 0.03333 \text{ M}$$
  
 $5.6 \times 10^{-10} = \frac{x^2}{0.03333 - x}$  (Assume  $0.03333 - x \sim 0.03333$ )  
 $5.6 \times 10^{-10} = \frac{x^2}{0.03333}$   
 $x = [\text{H}^+] = 4.320 \times 10^{-6}$   
pH =  $-\log(4.320 \times 10^{-6}) = 5.3645$ 

# e. 60.00 mL HCl

There have been  $(60 \text{ mL} \times 0.1 \text{ M}=) 6 \text{ mmol HCl}$  added to the flask.

	HCl	NH <sub>3</sub>	$\rightarrow$	NH <sub>4</sub> Cl
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)

[acid] = 
$$\frac{1 \text{ mmol}}{160 \text{ mL}} = 6.250 \times 10^{-3} \text{ M}$$

$$pH = -\log(6.250 \times 10^{-3}) = 2.2041$$