

Titration

We discussed strong acid-strong base titrations last semester.

Say we titrate HCl with NaOH

At the beginning of the titration, the pH is determined by the concentration of the acid.

After the end point of the titration, the pH is determined by the concentration of the base.

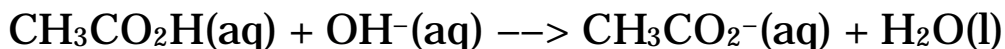
At the end point of the titration what is the pH?

At the endpoint the moles of HCl = the moles of NaOH so all that is present is H₂O, Cl⁻, and Na⁺. So, the pH is 7.

But what is different if a weak acid is titrated with a strong base?

Lets say we are titrating a solution of acetic acid, CH₃CO₂H, with sodium hydroxide, NaOH.

the reaction is



The sample of acetic acid is 25 mL of a 0.1 M acetic acid solution. It will be titrated with 0.1 M NaOH.

What is the pH before any base has been added?

just an equilibrium problem...

	CH ₃ CO ₂ H	H ⁺	CH ₃ CO ₂ ⁻
init	0.10	~0	0
change	- x	+ x	+ x
equilibrium	0.10 - x	x	x

$$1.8 \times 10^{-5} = \frac{x^2}{(0.10 - x)}$$

$$x = 0.0013$$

$$[\text{H}^+] = 0.0013 \quad \text{pH} = 2.87$$

What is the pH of the solution at the end point?

At the endpoint mol of NaOH = mol CH₃CO₂H. What is present in the solution?

Na⁺, and CH₃CO₂⁻, (the OH⁻ consumed the H⁺)

Na⁺ is neither an acid nor a base, but acetate is a base! So the pH is not 7! We have a base equilibrium problem.

So, what is the concentration of the base?

How many moles of acetate are present?

One mole of acetic acid produce one mole of acetate; so,

$$0.025 \text{ L CH}_3\text{CO}_2\text{H} \times \frac{0.1 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \text{ L soln}} = 0.0025 \text{ mol CH}_3\text{CO}_2\text{H}$$

$$0.0025 \text{ mol CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol CH}_3\text{CO}_2\text{H}}{1 \text{ mol CH}_3\text{CO}_2^-} = 0.0025 \text{ mol CH}_3\text{CO}_2^-$$

So, what volume is the acetate in? Not 25 mL you added a solution of NaOH.

how much base did you add? 1 mol acid for 1 mol base

$$0.0025 \text{ mol CH}_3\text{CO}_2\text{H} \times \frac{1 \text{ mol NaOH}}{1 \text{ mol CH}_3\text{CO}_2\text{H}} = 0.0025 \text{ mol NaOH}$$

where did the NaOH come from? a 0.1 M NaOH solution

$$\frac{0.0025 \text{ mol NaOH} \times 1 \text{ L of solution}}{0.1 \text{ mol NaOH}} = 0.025 \text{ L NaOH}$$

so, total volume is

$$\text{total vol} = \text{vol acid} + \text{vol titrant}$$

$$\text{vol} = 0.025 \text{ L} + 0.025 \text{ L} = 0.050 \text{ L}$$

So, the concentration is

$$\frac{0.0025 \text{ mol CH}_3\text{CO}_2^-}{0.050 \text{ L}} = 0.050 \text{ M}$$

Now finally the equilibrium problem!

	CH_3CO_2^-	$\text{CH}_3\text{CO}_2\text{H}$	OH^-
init	0.050	0	~0
change	- x	+ x	+ x
equilibrium	0.050 - x	x	x

$$K_b = \frac{x^2}{(0.050 - x)}$$

remember $K_w = K_b K_a$ $10^{-14} = K_b (1.8 \times 10^{-5})$

$$K_b = 5.56 \times 10^{-10}$$

$$5.56 \times 10^{-10} = \frac{x^2}{(0.050 - x)}$$

small x approximation

$$x^2 = 2.78 \times 10^{-11}$$

$$x = 5.27 \times 10^{-6}$$

$$[\text{OH}^-] = 5.27 \times 10^{-6}$$

so, $[\text{H}^+]$

$$[\text{H}^+][\text{OH}^-] = 10^{-14}$$

$$[\text{H}^+] = 10^{-14}/(5.27 \times 10^{-6})$$

$$[\text{H}^+] = 1.90 \times 10^{-9}$$

$$\text{pH} = 8.72$$

Say we stop the titration at 13 mL NaOH. What is the pH?

What is in solution after 13 mL NaOH have been added?

Na, CH_3CO_2^- , and $\text{CH}_3\text{CO}_2\text{H}$

Hey, this is a buffer problem! Both the acid and its conjugate base are present!

What are the concentrations?

moles of $\text{CH}_3\text{CO}_2\text{H}$?

Started with 0.0025 mol $\text{CH}_3\text{CO}_2\text{H}$ and some of it was consumed by the NaOH

so, how much NaOH was added?

$$0.013 \text{ L NaOH soln} \times \frac{0.01 \text{ mol NaOH}}{1 \text{ L NaOH soln}} = 0.0013 \text{ mol NaOH}$$

one mole $\text{CH}_3\text{CO}_2\text{H}$ consumed and one mole of CH_3CO_2^- formed for every mole of OH^- added

	$\text{CH}_3\text{CO}_2\text{H}$	OH^-	CH_3CO_2^-
start	0.0025	0.0013	0
rxn	- 0.0013	- 0.0013	+ 0.0013
after rxn	0.0012	~ 0	0.0013

Two ways to solve this

use Henderson-Haasbalch

$$\text{pH} = \text{pK}_a + \log(0.0013/0.0012)$$

$$\text{pH} = 4.75 + \log(1.08)$$

$$\text{pH} = 4.74 + 0.0347$$

$$\text{pH} = 4.78$$

solve as equilibrium

	$\text{CH}_3\text{CO}_2\text{H}$	CH_3CO_2^-	H^+
I	0.0012/0.038 L	0.0013/0.038 L	~0
C	- x	+ x	+ x
E	0.0316 - x	0.0342 + x	x

$$K_a = x(0.0342 + x)/(0.0316 - x)$$

small x approximation

$$1.8 \times 10^{-5} = x(1.08)$$

$$[\text{H}^+] = 1.67 \times 10^{-5} \Rightarrow \text{pH} = 4.78$$

notice that if we had gone exactly halfway to the endpoint, added 0.00125 mol OH^- , $\text{pH} = \text{pK}_a$

What happens if excess base has been added?

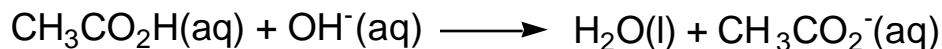
Say 37 mL 0.1 M NaOH have been added; what is the pH?

what is in solution

Na^+ , CH_3CO_2^- , and OH^-

what are the concentrations of all these things

$$0.037 \text{ L NaOH} \times \frac{0.10 \text{ mol NaOH}}{1 \text{ L}} = 0.0037 \text{ mol OH}^-$$



	$\text{CH}_3\text{CO}_2\text{H}$	OH^-	CH_3CO_2^-
S	0.0025	0.0037	0
R	-0.0025	-0.0025	+0.0025
AR	0.0000	0.0012	0.0025

$$\frac{0.0012 \text{ mol OH}^-}{(0.025 \text{ L} + 0.037 \text{ L})} = 0.0194 \text{ M OH}^-$$

$\frac{0.0025 \text{ mol CH}_3\text{CO}_2^-}{(0.025 \text{ L} + 0.037 \text{ L})} = 0.040 \text{ M CH}_3\text{CO}_2^-$ but K_b is 5.56×10^{-10} so OH^- from acetate is very small.
At the endpoint acetate produced only 10^{-6} M OH^-

So, pH is determined by the concentration of excess NaOH!

$$10^{-14} = [\text{H}^+][\text{OH}^-]$$

$$[\text{H}^+] = 10^{-14}/(0.0194)$$

$$[\text{H}^+] = 5.167 \times 10^{-13}$$

$$\text{pH} = 12.29$$

Prove weak base doesn't matter



CH_3CO_2^-	$\text{CH}_3\text{CO}_2\text{H}$	OH^-
0.0025 mol/0.062	0	0.0012/0.062
-x	+x	+x
0.0025/0.062 - x	x	0.0012/0.062 + x

$$5.56 \times 10^{-10} = \frac{x (0.0012/0.062 + x)}{(0.0025/0.062 - x)}$$

small x approximation

$$5.56 \times 10^{-10} = \frac{x (0.0012/0.062)}{(0.0025/0.062)}$$

$$x = 1.1583 \times 10^{-9}$$

$$[\text{OH}^-] = 0.0012/0.062 + 1.1582 \times 10^{-9}$$

$$[\text{OH}^-] = 0.0193548387097$$

$$+ \underline{0.0000000011582}$$

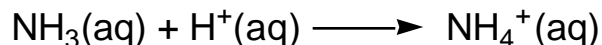
$$[\text{OH}^-] = 0.0193548398679$$

What do you think? Is the [OH⁻] contribution from the acetate significant?

Add 25 mL of a 0.10 M HCl solution to 20.0 mL of a 0.10 M NH₃ solution.

This is a strong acid weak base titration. We assume that the strong acid reacts with the weak base completely; then we analyze that which remains in solution.

The reaction is



	NH ₃	H ⁺	NH ₄ ⁺
S	0.0020 mol	0.0025 mol	0
R	-0.0020	-0.0020	+0.0020
AR	0	0.0005	0.0020

So, some strong acid and some weak acid remain in solution.



Do we need to solve this equilibrium problem?

No, $[\text{H}^+] = 0.0005/(0.045) = 0.011 \text{ M}$ why....since there is so much H⁺ already present the ammonium ion does not ionize much.

The increase in $[\text{H}^+]$ caused by the ammonium ion is $2.24 \times 10^{-9} \text{ M}$. 2.24×10^{-9} is insignificant as compared to the 0.011 M H^+ already present.