

Slide 1

What's in your beaker?

Slide 2

What's a titration?

A titration is a chemical reaction conducted with a controlled addition of one of the reactants. By carefully monitoring the amount of the reactant added, we can figure out how much of the other reactant must have been there.

Slide 3

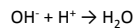
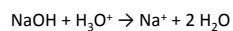
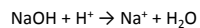
Titration example

50.00 mL of an unknown acid is titrated with 0.1234 M NaOH. It required 22.67 mL of titrant to reach the endpoint. What was the pH of the original acid solution?

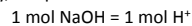
Like all chemistry problems, we begin with...

Slide 4

A BALANCED EQUATION!



Either way, the point is:



Slide 5

Titration example

50.00 mL of an unknown acid is titrated with 0.1234 M NaOH. It required 22.67 mL of titrant to reach the endpoint. What was the pH of the original acid solution?

$$0.1234 \text{ M NaOH} * 22.67 \text{ mL NaOH} = ? \text{ M H}^+ * 50.00 \text{ mL H}^+$$

$$5.595 \times 10^{-2} \text{ M H}^+$$

$$\text{pH} = -\log(5.595 \times 10^{-2} \text{ M}) = 1.25$$

Slide 6

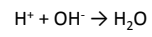
How does a titration actually occur?

You add one reactant (NaOH in this case) drop by drop until the other reactant (H⁺ in this case) is completely reacted (neutralized).

How do you know the reaction is over?

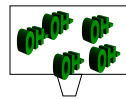
Some kind of indicator: another chemical compound, pH.

Slide 7



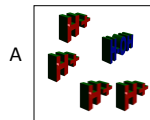
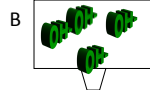
As I make water, by adding OH^- to H^+ (or H^+ to OH^-), the pH changes.

Slide 8



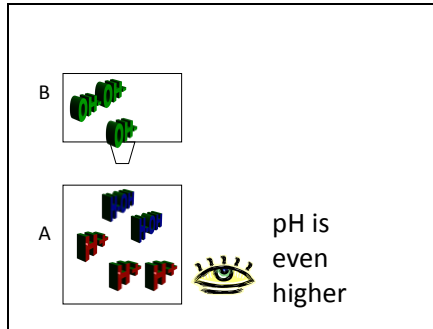
pH is low

Slide 9

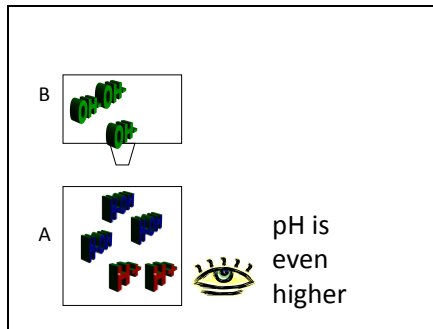


pH is
getting
higher

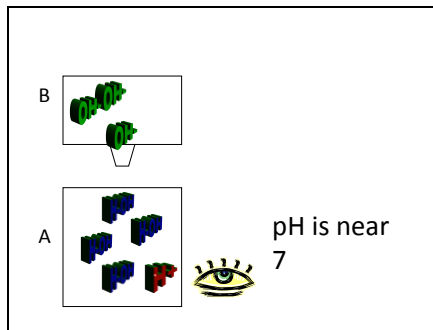
Slide 10



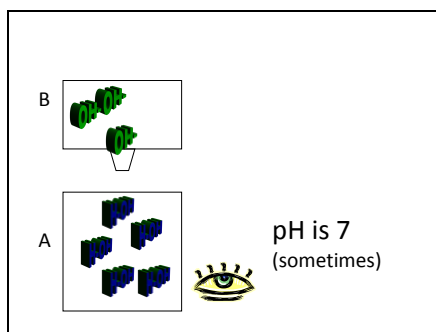
Slide 11



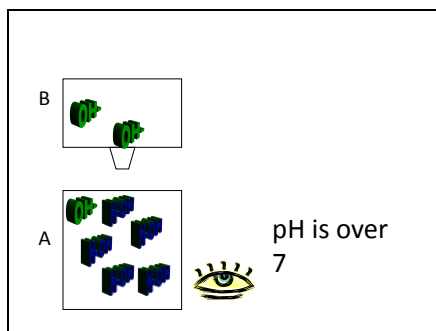
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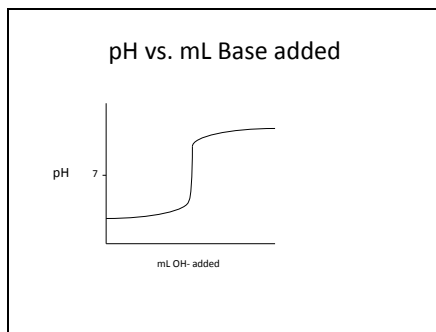
Slide 13



Slide 14



Slide 15



Slide 16

Could we calculate the pH all along the way?

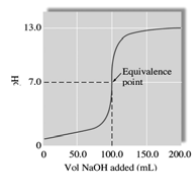
Sure, why not? It's all a question of what's in the beaker!

Slide 17

Potentiometric Titrations

A potentiometric titration combines a titration with a pH measurement. A graph of pH vs. titrant volume is called a titration curve.

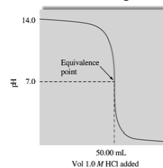
The equivalence point (stoichiometric point) occurs when moles of base (B or A^-) = moles of H^+ donated by the acid (HA or BH^+).



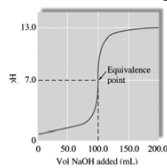
Slide 18

Strong Acid - Strong Base Titrations

Analyte is strong base
Titrant is a strong acid



Analyte is strong acid
Titrant is a strong base



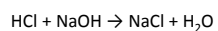
Slide 19

50.00 mL of 0.100 M HCl is titrated with 0.100 M NaOH. Calculate the pH at 10.0 mL increments from 0.00 mL titrant added until 100.0 mL of titrant.

We begin with...

Slide 20

A Balanced Equation!



At 0.00 mL added, what's in the beaker?

50.00 mL of 0.100 M HCl

– nothing but HCl and H₂O

Slide 21

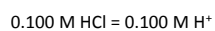
pH of 50.00 mL of 0.100 M HCl

What do we know about HCl?

It's a strong acid!

What do we know about strong acids?

They completely dissociate.



$$\text{pH} = -\log(0.100 \text{ M H}^+) = 1.0$$

Slide 22

Add 10.0 mL of 0.100 M NaOH

	HCl	+	NaOH	→	NaCl	+	H ₂ O
Start	0.005 mol		0		0		LOTS
Add			.001 mol				

What does NaOH do?
Neutralizes HCl.
How much HCl?
0.001 mol HCl

Slide 23

Add 10.0 mL of 0.100 M NaOH

	HCl	+	NaOH	→	NaCl	+	H ₂ O
I	0.005 mol		0.001 mol		0		LOTS
C	- 0.001 mol		-0.001 mol		+0.001 mol		+0.001
=	0.004 mol		0 mol		0.001 mol		LOTS

So the pH is....?

$$pH = -\log\left(\frac{0.004 \text{ mol}}{0.060 \text{ L}}\right) = 1.17$$

Slide 24

Add another 10.0 mL of 0.100 M NaOH

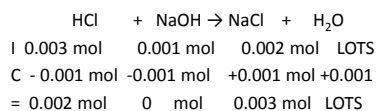
	HCl	+	NaOH	→	NaCl	+	H ₂ O
I	0.004 mol		0.001 mol		0.001 mol		LOTS
C	- 0.001 mol		-0.001 mol		+0.001 mol		+0.001
=	0.003 mol		0 mol		0.002 mol		LOTS

So the pH is....

$$pH = -\log\left(\frac{0.003 \text{ mol}}{0.070 \text{ L}}\right) = 1.37$$

Slide 25

Add another 10.0 mL of 0.100 M NaOH

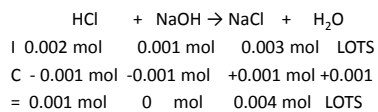


So the pH is....

$$pH = -\log\left(\frac{0.002 \text{ mol}}{0.080 \text{ L}}\right) = 1.60$$

Slide 26

Add another 10.0 mL of 0.100 M NaOH

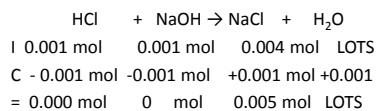


So the pH is....

$$pH = -\log\left(\frac{0.001 \text{ mol}}{0.090 \text{ L}}\right) = 1.95$$

Slide 27

Add another 10.0 mL of 0.100 M NaOH



So the pH is....

$$pH = -\log\left(\frac{0.000 \text{ mol}}{0.100 \text{ L}}\right) = \text{WTF?}$$

Slide 28

WHAT'S IN THE BEAKER?

$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 I 0.001 mol 0.001 mol 0.004 mol LOTS
 C - 0.001 mol -0.001 mol +0.001 mol +0.001
 = 0.000 mol 0 mol 0.005 mol LOTS
 NO HCl, so NO H^+ from there. I have NaCl which is...
 A salt
 Acidic or basic?
 Neither
 What else is in the beaker?
 Water
 So what?
 K_w

Slide 29

Add another 10.0 mL of 0.100 M NaOH

$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 I 0.001 mol 0.001 mol 0.004 mol LOTS
 C - 0.001 mol -0.001 mol +0.001 mol +0.001
 = 0.000 mol 0 mol 0.005 mol LOTS

 So the pH is....
 $pH = 7$

Slide 30

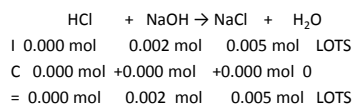
Add another 10.0 mL of 0.100 M NaOH

$\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$
 I 0.000 mol 0.001 mol 0.005 mol LOTS
 C 0.000 mol +0.000 mol +0.000 mol 0
 = 0.000 mol 0.001 mol 0.005 mol LOTS

 So the pH is....
 $14 - pOH = 14 - \left(-\log \left(\frac{.001 \text{ mol}}{0.110 \text{ L}} \right) \right) = 11.96$

Slide 31

Add another 10.0 mL of 0.100 M NaOH



So the pH is....

$$14 - pOH = 14 - \left(-\log \left(\frac{.002 \text{ mol}}{0.120 \text{ L}} \right) \right) = 12.22$$

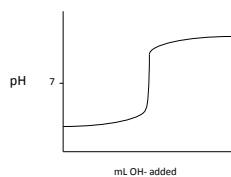
Slide 32

Summarizing

mL 0.100 M NaOH added	pH
0	1.00
10	1.17
20	1.37
30	1.60
40	1.95
50	7
60	11.96
70	12.22
80	12.36
90	12.46
100	12.52

Slide 33

pH vs. mL Base added



Slide 34

Do they all look like that?

No, it depends on what's in the beaker!

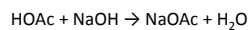
Slide 35

50.00 mL of 0.100 M HOAc is titrated with 0.100 M NaOH. Calculate the pH at 10.0 mL increments from 0.00 mL titrant added until 100.0 mL of titrant.

We begin with...

Slide 36

A Balanced Equation!



At 0.00 mL added, what's in the beaker?

50.00 mL of 0.100 M HOAc

– nothing but HOAc and H₂O

Slide 37

pH of 50.00 mL of 0.100 M HOAc

What do we know about HOAc?

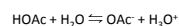
It's a weak acid!

What do we do about weak acids?

Equilibrium, baby! 3 parts!

Slide 38

$$K_a = 1.8 \times 10^{-5}$$



	0.100 M	-	0	0
I				
C	-x	-	+x	+x
E	0.100-x	-	x	x

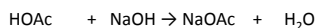
$$1.8 \times 10^{-5} = \frac{[x][x]}{0.100-x}$$

$$x = 1.34 \times 10^{-3} \text{ M}$$

$$\text{pH} = -\log(1.34 \times 10^{-3} \text{ M}) = 2.87$$

Slide 39

Add 10.0 mL of 0.100 M NaOH



I	0.005 mol	0.001 mol	0	LOTS
C	- 0.001 mol	-0.001 mol	+0.001 mol	+0.001
=	0.004 mol	0 mol	0.001 mol	LOTS

$$[\text{HOAc}] = \frac{0.004 \text{ mol}}{0.060 \text{ L}} = 6.67 \times 10^{-2} \text{ M}$$

And then....WHAT'S IN THE BEAKER?

Slide 40

$K_a = 1.8 \times 10^{-5}$

$\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{OAc}^- + \text{H}_3\text{O}^+$

I	0.0667	-	0.0167	0
C	M		M	
E	-x	-	+x	+x
	0.0667-x	-	0.0167+x	x

What is this?

It's a BUFFER!!!

Slide 41

$K_a = 1.8 \times 10^{-5}$

$\text{HOAc} + \text{H}_2\text{O} \rightleftharpoons \text{OAc}^- + \text{H}_3\text{O}^+$

I	0.0667	-	0.0167	0
C	M		M	
E	-x	-	+x	+x
	0.0667-x	-	0.0167+x	x

$pH = pK_a + \log \frac{[\text{base}]}{[\text{Acid}]}$

$pH = 4.74 + \log \frac{[0.0167]}{[0.0667]} = 4.14$

Slide 42

Add another 10.0 mL of 0.100 M NaOH

$\text{HOAc} + \text{NaOH} \rightarrow \text{NaOAc} + \text{H}_2\text{O}$

I	0.004 mol	0.001 mol	0.001 mol	LOTS
C	- 0.001 mol	-0.001 mol	+0.001 mol	+0.001
=	0.003 mol	0 mol	0.002 mol	LOTS

$pH = 4.74 + \log \frac{[0.002 \text{ mol}]}{[0.003 \text{ mol}]} = 4.56$

Slide 43

Add another 10.0 mL of 0.100 M NaOH

	HOAc	+	NaOH	→	NaOAc	+	H ₂ O
I	0.003 mol		0.001 mol		0.002 mol		LOTS
C	- 0.001 mol		-0.001 mol		+0.001 mol		+0.001
=	0.002 mol		0 mol		0.003 mol		LOTS

$$pH = 4.74 + \log \frac{[0.003 \text{ mol}]}{[0.002 \text{ mol}]} = 4.92$$

Slide 44

Add another 10.0 mL of 0.100 M NaOH

	HOAc	+	NaOH	→	NaOAc	+	H ₂ O
I	0.002 mol		0.001 mol		0.003 mol		LOTS
C	- 0.001 mol		-0.001 mol		+0.001 mol		+0.001
=	0.001 mol		0 mol		0.004 mol		LOTS

$$pH = 4.74 + \log \frac{[0.004 \text{ mol}]}{[0.001 \text{ mol}]} = 5.34$$

Slide 45

Add another 10.0 mL of 0.100 M NaOH

	HOAc	+	NaOH	→	NaOAc	+	H ₂ O
I	0.001 mol		0.001 mol		0.004 mol		LOTS
C	- 0.001 mol		-0.001 mol		+0.001 mol		+0.001
=	0.000 mol		0 mol		0.005 mol		LOTS

$$pH = 4.74 + \log \frac{[0.005 \text{ mol}]}{[0.000 \text{ mol}]} = \text{WTF?}$$

Is the pH = 7?

Slide 46

WHAT'S IN THE BEAKER?

$\text{HOAc} + \text{NaOH} \rightarrow \text{NaOAc} + \text{H}_2\text{O}$
 I 0.001 mol 0.001 mol 0.004 mol LOTS
 C - 0.001 mol -0.001 mol +0.001 mol +0.001
 = 0.000 mol 0 mol 0.005 mol LOTS

I have NaOAc which is...

A salt

Acidic or basic?

NaOH is a strong base, HOAc is a weak acid. OAc⁻ is a weak base.

Slide 47

OMG IT'S A K_b PROBLEM!

$\text{OAc}^- + \text{H}_2\text{O} \rightleftharpoons \text{HOAc} + \text{OH}^-$
 $\begin{array}{c} \text{I} \frac{0.005 \text{ mol}}{0.100 \text{ L}} \\ \text{C} -x \\ \text{E } 0.05 \text{ M}-x \end{array} \quad \begin{array}{c} - \\ - \\ x \end{array} \quad \begin{array}{c} 0 \\ +x \\ x \end{array} \quad \begin{array}{c} 0 \\ +x \\ x \end{array}$

$$K_b = \frac{K_w}{K_a} = 5.56 \times 10^{-10} = \frac{[x][x]}{0.05 - x}$$

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

$$\text{pOH} = -\log(5.27 \times 10^{-6}) = 5.28$$

$$\text{pH} = 14 - 5.28 = 8.72$$

Slide 48

Add another 10.0 mL of 0.100 M NaOH

Now it's just all about the excess NaOH!

Just like before.

Slide 49

Summarizing	
mL 0.100 M NaOH added	pH
0	2.87
10	4.14
20	4.56
30	4.92
40	5.34
50	8.72
60	11.96
70	12.22
80	12.36
90	12.46
100	12.52

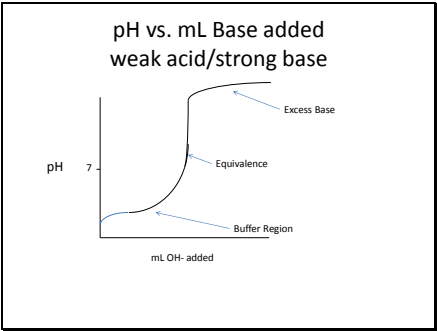
Slide 50

Comparing

mL 0.100 M NaOH weak acid	pH
0	2.87
10	4.14
20	4.56
30	4.92
40	5.34
50	8.72
60	11.96
70	12.22
80	12.36
90	12.46
100	12.52

mL 0.100 M NaOH Strong acid	pH
0	1.00
10	1.17
20	1.37
30	1.60
40	1.95
50	7
60	11.96
70	12.22
80	12.36
90	12.46
100	12.52

Slide 51



Slide 52

CB If benzoic acid, $pK_a = 4.05$, is titrated with NaOH(aq) , the equivalence point is:

- A. Acidic if the initial concentration of acid was higher than that of base.
- B. Always Acidic
- C. Basic if the initial concentration of base was higher than that of acid.
- D. Always Basic
- E. Neutral

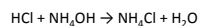
Slide 53

CB If methyl amine, $pK_b = 9.2$, is titrated with HCl(aq) , the equivalence point is:

- A. Acidic if the initial concentration of acid was higher than that of base.
- B. Always Acidic
- C. Basic if the initial concentration of base was higher than that of acid.
- D. Always Basic
- E. Neutral

Slide 54

The reverse happens with a weak base/strong acid



When you start adding base, you've got excess strong acid, so only $[\text{HCl}]$ matters - "excess strong acid"

At equivalence, you have an acidic salt, so the pH is less than 7.

After equivalence, you've got a weak base and its conjugate acid - buffer region!
