

## Chemical Equilibria: common ion effect, buffers, and titration

Syllabus Learning Outcomes : 6, 7

1

49

## pH before, during, & at equivalence point of reaction

- **Strong acid + strong base**  
HCl + NaOH →  
Ka(HCl) = large  
Kb(NaOH) = large
- **Strong acid + weak base**  
HCl + NH<sub>3</sub> →  
Kb(NH<sub>3</sub>) = 1.8 × 10<sup>-5</sup>
- **Weak acid + strong base**  
HOAc + NaOH →  
Ka(HOAc) = 1.8 × 10<sup>-5</sup>
- **Weak acid + weak base**  
HOAc + NH<sub>3</sub> →  
Compare Ka, Kb to  
determine pH at  
equivalence point

Dr. Michael Love (2) © 2007

2

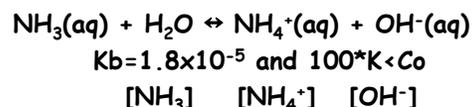
## pH at equivalence point

- **Strong acid + strong base**  
HCl + NaOH →  
Ka(HCl) = Kb(NaOH) →  
neutral at equivalence
- **Strong acid + weak base**  
HCl + NH<sub>3</sub> →  
Ka(HCl) > Kb(NH<sub>3</sub>) →  
acidic at equivalence
- **Weak acid + strong base**  
HOAc + NaOH →  
Kb(NaOH) > Ka(HOAc) →  
basic at equivalence
- **Weak acid + weak base**  
HOAc + NH<sub>3</sub> →  
Ka(HOAc) = Kb(NH<sub>3</sub>) →  
neutral at equivalence

Dr. Michael Love (3) © 2007

3

What is the pH of 0.25M NH<sub>3</sub>(aq)?



initial  
change  
equilib.

Dr. Michael Love (4) © 2007

4

What is the pH of 0.25M NH<sub>3</sub>(aq)?



$$K_b = 1.8 \times 10^{-5} \text{ and } 100 \cdot K < C_0$$



initial    0.25    0    0

change    -x    x    x

equilib    0.25-x    x    x

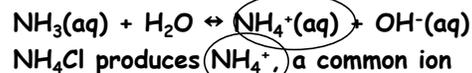
$$1.8 \times 10^{-5} = x^2 / 0.25, \quad x = [\text{OH}^-] = 0.0021\text{M}$$

$$\text{pOH} = 2.67, \quad \text{pH} = 14.00 - 2.67 = 11.33$$

Dr. Michael Love (5) © 2007

5

How does pH of 0.25M NH<sub>3</sub>(aq)  
change after adding NH<sub>4</sub>Cl?



LeChatelier's principle predicts a shift  
to the \_\_\_\_\_?

NH<sub>4</sub><sup>+</sup> is a weak acid

pH goes \_\_\_\_\_?

Dr. Michael Love (6) © 2007

6

7

How does pH of 0.25M  $\text{NH}_3(\text{aq})$  change after adding  $\text{NH}_4\text{Cl}$ ?

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 $\text{NH}_4\text{Cl}$  produces  $\text{NH}_4^+$ , a common ion

LeChatelier's principle predicts a shift to the Left

$\text{NH}_4^+$  is a weak acid  
 pH goes Down

Dr. Michael Love (7) © 2007

8

What is the pH of a solution with 0.10M  $\text{NH}_4\text{Cl}$  and 0.25M  $\text{NH}_3(\text{aq})$ ?

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 pH should decrease

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
initial			
change			
equilib.			

Dr. Michael Love (8) © 2007

9

What is the pH of a solution with 0.10M  $\text{NH}_4\text{Cl}$  and 0.25M  $\text{NH}_3(\text{aq})$ ?

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 pH should decrease,  $100 \cdot K < C_0$

	$[\text{NH}_3]$	$[\text{NH}_4^+]$	$[\text{OH}^-]$
initial	0.25	0.10	0
change	-x	+x	+x
equilib.	0.25-x	0.10+x	x

Dr. Michael Love (9) © 2007

10

What is the pH of a solution with 0.10M  $\text{NH}_4\text{Cl}$  and 0.25M  $\text{NH}_3(\text{aq})$ ?

$\text{NH}_3(\text{aq}) + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$   
 $K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

$100 \cdot K < C_0$ , so  $1.8 \times 10^{-5} = \frac{[0.1][x]}{[0.25]}$   
 $x = [\text{OH}^-] = 4.5 \times 10^{-5}$   
 $\text{pOH} = 4.35$ ,  $\text{pH} = 9.65$

The pH drops from 11.33 to 9.65 by adding  $\text{NH}_4^+$ , a common ion

Dr. Michael Love (10) © 2007

11

Buffer solutions resist pH changes

HCl greatly changes the pH of pure water. For example, the pH changes 7.00 to pH 2.70 after adding 10mL of 0.1M HCl to 500mL water.

HCl slightly changes the pH of a weak acid HOAc and its conjugate base OAc<sup>-</sup>. For example, pH changes from 4.68 to 4.67 after adding 10mL of 0.1M HCl to 500mL of buffer containing 0.60M OAc<sup>-</sup> and 0.70M HOAc.

12

To make a buffer, add a weak acid to its conjugate base

HOAc	+	OAc <sup>-</sup>
$\text{NH}_4^+$	+	$\text{NH}_3$
$\text{H}_2\text{PO}_4^-$	+	$\text{HPO}_4^{2-}$

Buffers use the common ion effect

Dr. Michael Love (12) © 2007

## Buffers work because:

- **weak acid** neutralizes added base
  - **weak base** neutralizes added acid
- K for adding strong acid and base to buffer is the reverse of these reactions:
- $$\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}, K_a = 6.2 \times 10^{-8}$$
- $$\text{HPO}_4^{2-} + \text{H}_2\text{O} \rightarrow \text{OH}^- + \text{H}_2\text{PO}_4^-, K_b = 1.6 \times 10^{-7}$$
- $1/K_a = 1.6 \times 10^7$ , so added acids become  $\text{H}_2\text{PO}_4^-$   
 $1/K_b = 6.3 \times 10^6$ , so added bases become  $\text{HPO}_4^{2-}$   
 pH ~fixed as long as  $\text{H}_2\text{PO}_4^-$  and  $\text{HPO}_4^{2-}$  remain

Dr. Michael Love (13) © 2007

Calculate the pH of a solution with 0.70M HOAc and 0.60M OAc<sup>-</sup>

$\text{HOAc} + \text{H}_2\text{O} \rightarrow \text{OAc}^- + \text{H}_3\text{O}^+$ ,  $K_a = 1.8 \times 10^{-5}$   
 If 0.70M HOAc has pH 2.45, is this buffer pH higher or lower \_\_\_\_\_?

[HOAc] [OAc<sup>-</sup>] [H<sub>3</sub>O<sup>+</sup>]

initial  
change  
equilib.

Dr. Michael Love (14) © 2007

Calculate the pH of a solution with 0.70M HOAc and 0.60M OAc<sup>-</sup>

$\text{HOAc} + \text{H}_2\text{O} \rightarrow \text{OAc}^- + \text{H}_3\text{O}^+$ ,  $K_a = 1.8 \times 10^{-5}$   
 $100 * K < C_0$

	[HOAc]	[OAc <sup>-</sup> ]	[H <sub>3</sub> O <sup>+</sup> ]
initial	0.70	0.60	0
change	-x	+x	+x
equilib.	0.70-x	0.60+x	x

$K_a = 1.8 \times 10^{-5} = \frac{[0.60][x]}{[0.70]}$   
 $x = [\text{H}_3\text{O}^+] = 2.1 \times 10^{-5}$ , pH = 4.68

Dr. Michael Love (15) © 2007

## Henderson-Hasselbalch approximation

When  $100 * K < C_0$ , the equilibrium expressions are:

For acids  $K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$  For bases  $K_b = \frac{[\text{OH}^-][\text{BH}^+]}{[\text{B}]}$

$[\text{H}_3\text{O}^+] = K_a \frac{[\text{HA}]}{[\text{A}^-]}$   $[\text{OH}^-] = K_b \frac{[\text{B}]}{[\text{BH}^+]}$

$\text{pH} = \text{p}K_a - \log\left(\frac{[\text{HA}]}{[\text{A}^-]}\right)$   $\text{pOH} = \text{p}K_b - \log\left(\frac{[\text{B}]}{[\text{BH}^+]}\right)$

For acids, the pH is set by the pKa and adjusted by the ratio of HA to A<sup>-</sup>.

For bases, the pOH is set by the pKb and adjusted by the ratio of B to BH<sup>+</sup>

Dr. Michael Love (16) © 2007

Calculate the pH when 1.00mL of 1.00M HCl is added to

- 0.500L of water, pH=7 initially
- 0.500L of buffer with [HOAc]=0.700 M and [OAc<sup>-</sup>]=0.600M (pH = 4.68)

Part a: Calculate [H<sub>3</sub>O<sup>+</sup>]

For a strong acid, [H<sub>3</sub>O<sup>+</sup>]=[HCl], so use

$$M_{\text{conc}} \cdot V_{\text{conc}} = M_{\text{dil}} \cdot V_{\text{dil}}$$

$$M_{\text{dil}} = [\text{H}_3\text{O}^+] = 2.00 \times 10^{-3} \text{ M}$$

$$\text{pH} = 2.70$$

Dr. Michael Love (17) © 2007

Calculate the pH when 1.00mL of 1.00M HCl is added to buffer

Part b: Stoichiometry, volume, ICE

Step 1: Stoichiometry (0.001mol H<sub>3</sub>O<sup>+</sup>)

React strong acid with buffer ( $K_{\text{rxn}}$  big).



Before rxn

Change

After rxn

Dr. Michael Love (18) © 2007

19  
Calculate the pH when 1.00mL of 1.00M HCl is added to buffer

Part b: Stoichiometry, volume, ICE

Step 1: Stoichiometry (0.001mol H<sub>3</sub>O<sup>+</sup>)

Entries in table are mol = M\*V!

	[H <sub>3</sub> O <sup>+</sup> ]	[OAc <sup>-</sup> ]	[HOAc]
Before rxn	0.001	0.300	0.350
Change	-0.001	-0.001	+0.001
After rxn	0	0.299	0.351

Dr. Michael Love (19) © 2007

20  
Calculate the pH when 1.00mL of 1.00M HCl is added to buffer

Part b: Stoichiometry, volume, ICE

Step 2: Calculate new volume, V=0.501L

Step 3: Get new [ ]=mol/V for ICE table

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

	[HOAc]	[H <sub>3</sub> O <sup>+</sup> ]	[OAc <sup>-</sup> ]
Initial	0.701	0	0.597
Change	-x	+x	+x
Equilib.	0.701-x	x	0.597+x

Dr. Michael Love (20) © 2007

21  
Calculate the pH when 1.00mL of 1.00M HCl is added to buffer

$$K_a = [\text{H}_3\text{O}^+][\text{OAc}^-]/[\text{HOAc}] = 1.8 \times 10^{-5}$$

Because  $100 \cdot K < C_0$ ,

$$[x][0.597]/[0.701] = 1.8 \times 10^{-5}$$

$$x = [\text{H}_3\text{O}^+] = 2.11 \times 10^{-5}$$

pH=4.67, pH changes by 0.01 unit

Dr. Michael Love (21) © 2007

22  
Prepare 0.50L of buffer at pH 4.30

Step 1. Select the buffer system so that pH=pKa or [H<sub>3</sub>O<sup>+</sup>]=10<sup>-pH</sup>

$$[\text{H}_3\text{O}^+] = 10^{-4.30} = 5.01 \times 10^{-5}$$

Acid/base	K <sub>a</sub>	pK <sub>a</sub>
HSO <sub>4</sub> <sup>-</sup> /SO <sub>4</sub> <sup>2-</sup>	1.2 × 10 <sup>-2</sup>	1.92
HOAc/OAc <sup>-</sup>	1.8 × 10 <sup>-5</sup>	4.74
HCN/CN <sup>-</sup>	4.0 × 10 <sup>-10</sup>	9.40

Dr. Michael Love (22) © 2007

23  
Prepare 0.50L of buffer at pH 4.30

Step 2. Calculate [OAc<sup>-</sup>]/[HOAc] ratio using HH or equilibrium method.

$$K_a = [\text{H}_3\text{O}^+][\text{OAc}^-]/[\text{HOAc}] = 1.8 \times 10^{-5}$$

$$[5.01 \times 10^{-5}][\text{OAc}^-]/[\text{HOAc}] = 1.8 \times 10^{-5}$$

$$[\text{OAc}^-]/[\text{HOAc}] = 0.359$$

Dr. Michael Love (23) © 2007

24  
Prepare 0.50L of buffer at pH 4.30

Step 3. Determine [HOAc] and [OAc<sup>-</sup>].

$$[\text{OAc}^-]/[\text{HOAc}] = 0.359.$$

If [HOAc]=1.00M, [OAc<sup>-</sup>]=0.359M

Step 4. Determine amounts.

To make 0.50L of sol'n, need 0.500mol HOAc and 0.180mol OAc<sup>-</sup>.

Step 5. To get lab amounts, would need MM or [ ] for the reagents.

Dr. Michael Love (24) © 2007

25  
**Diluting a buffer solution with water does not change pH until the assumption,  $100 \cdot K_a < C_0$ , fails**

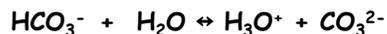
When the assumption ( $100 \cdot K_a < C_0$ ) holds, pH depends on the ratio of [acid] to [conjugate base], not the concentration.

Commercially available buffers give directions to prepare.

Dr. Michael Love (25) © 2007

26  
**Calculate the pH of this buffer at home**

8.0g of  $\text{NaHCO}_3$  and 16.0g of  $\text{Na}_2\text{CO}_3$ .



What additional information do you need?

- Prepare 1.00L buffer
- $K_a$  for  $\text{HCO}_3^-$  is  $4.8 \times 10^{-11}$

Dr. Michael Love (26) © 2007

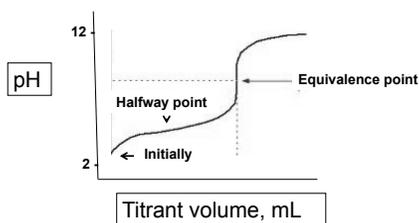
27  
**Calculate the pH of this buffer at home**

8.0g of  $\text{NaHCO}_3$  and 16.0g of  $\text{Na}_2\text{CO}_3$ .

Using the previous data, the pH would be 10.52

Dr. Michael Love (27) © 2007

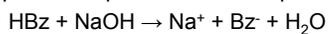
28  
Calculate the pH from titrating 100. mL of 0.025M benzoic acid with 0.100M NaOH at these key points: initially, halfway point, equivalence point.



The calculation for pH initially would follow the format of the examples for pH of a weak acid from last lecture.

29  
**Acid-Base Titration**

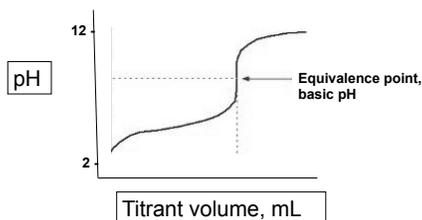
QUESTION: Titrate 100. mL of a 0.025 M solution of benzoic acid with 0.100 M NaOH to the equivalence point. What is the pH?



The pH of the final solution will be

1. Less than 7
2. Equal to 7
3. Greater than 7

30  
Titrate 100. mL of 0.025M benzoic acid with 0.100 M NaOH to the equivalence point.



Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH at the equivalence point?

**Strategy** — find the *concentration* of the conjugate base  $Bz^-$  in the solution AFTER the titration, then calculate pH.

This is a two-step problem

1. stoichiometry of acid-base reaction
2. equilibrium calculation

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH at the equivalence point?

Step 1: Stoichiometry

A. Calc. moles of NaOH req' d

$$(0.100 \text{ L HBz})(0.025 \text{ M}) = 0.0025 \text{ mol HBz}$$

This requires 0.0025 mol NaOH

B. Calc. volume of NaOH req' d

$$0.0025 \text{ mol} (1 \text{ L} / 0.100 \text{ mol}) = 0.025 \text{ L}$$

25 mL of NaOH req' d

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH at the equivalence point?

Step 1: Stoichiometry

25 mL of NaOH req' d

C. Moles of  $Bz^-$  produced = moles HBz = 0.0025 mol

D. Calc. conc. of  $Bz^-$

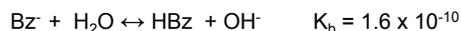
There are 0.0025 mol of  $Bz^-$  in a TOTAL SOLUTION VOLUME of 125 mL

$$[Bz^-] = 0.0025 \text{ mol} / 0.125 \text{ L} = 0.020 \text{ M}$$

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH at equivalence point?

Step 2: Equivalence Point

At equivalence point,  $Bz^-$  determines the pH because it is the only species remaining.



	[Bz <sup>-</sup> ]	[HBz]	[OH <sup>-</sup> ]
initial	0.020	0	0
change	- x	+x	+x
equilib	0.020-x	x	x

Titrate 100. mL of a 0.025M benzoic acid with 0.100M NaOH. What is the pH at equivalence point?

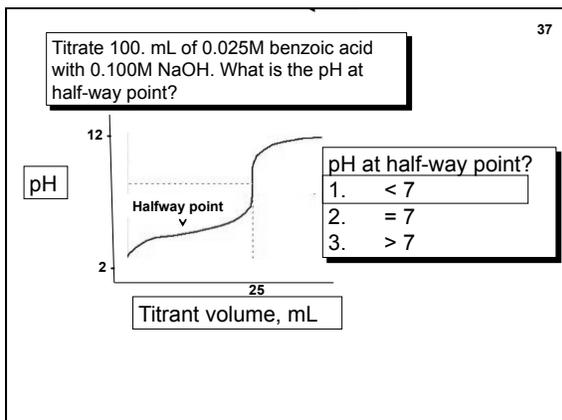
Step 2: Equivalence Point

$$K_b = 1.6 \times 10^{-10} = \frac{x^2}{0.020 - x}$$

$$x = [OH^-] = 1.8 \times 10^{-6}$$

$$pOH = 5.75 \text{ -----> } pH = 8.25$$

To do a titration, select an indicator that changes color at the equivalence point, one that changes at pH=8.25



38

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH at the half-way point?

$\text{HBz} + \text{H}_2\text{O} \leftrightarrow \text{H}_3\text{O}^+ + \text{Bz}^- \quad K_a = 6.3 \times 10^{-5}$

Both HBz and Bz<sup>-</sup> are present.  
This is a BUFFER!

$$[\text{H}_3\text{O}^+] = \frac{[\text{HBz}]}{[\text{Bz}^-]} \cdot K_a$$

At the half-way point,  $[\text{HBz}] = [\text{Bz}^-]$   
Therefore,  $[\text{H}_3\text{O}^+] = K_a = 6.3 \times 10^{-5}$   
 $\text{pH} = 4.20 = \text{p}K_a$  of the acid

39

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH after adding 15 mL of NaOH?

Step 1—Stoichiometry (Acid Base Rxn)

	$[\text{OH}^-]$	+	$[\text{HBz}]$	---->	$[\text{Bz}^-]$
Before rxn	0.0015 mol		0.0025 mol		0 mol
Change	-0.0015		-0.0015		+0.0015
After rxn	0 mol		0.0010 mol		0.0015 mol

Calculate new volume  
 $V = 100 \text{ ml (benzoic acid)} + 15 \text{ ml (NaOH)}$   
 $V = 115 \text{ mL}$

40

Titrate 100. mL of 0.025M benzoic acid with 0.100M NaOH. What is the pH after adding 15 mL of NaOH?

Step 2—Solve equilibrium expression

	$[\text{HBz}]$	---->	$[\text{H}_3\text{O}^+]$	+	$[\text{Bz}^-]$
Initial	0.0087 M		0 M		0.0130M
Change	-x		+x		+x
Equilibrium	0.0087-x		x		0.0130+x

Calculate  $\text{pH} = -\log[\text{H}_3\text{O}^+]$   
 $K_a = \frac{(x)(0.0130+x)}{(0.0087-x)} = 6.3 \times 10^{-5}$   
 $100 * K_a < 0.0087$ , so  $6.3 \times 10^{-5} = 0.0130x / 0.0087$   
 $\text{pH} = -\log[\text{H}_3\text{O}^+] = -\log[x] = -\log[4.22 \times 10^{-5}]$   
 $\text{pH} = 4.38$