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5.111 Principles of Chemical Science

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5.111 Lecture Summary #23
Acid/Base Equilibrium Continued Topic: Titrations

From Friday's handout

Acid buffer action: The weak acid, HA, transfers protons to OH^- ions supplied by strong base.
The conjugate base, A^-, of the weak acid accepts protons from the H_3O^+ ions supplied by a strong acid.

A strong acid and the salt of its conjugate base don't make a good buffer. Why?

Base Buffer Example: $NH_3\ (aq) + H_2O\ (l) \rightleftharpoons NH_4^+\ (aq) + OH^-\ (aq)$

When strong acid is added, NH_3 accepts protons from incoming acid to make NH_4^+. When strong base is added, NH_4^+ donates a proton to form NH_3 and H_2O. pH remains the same.

Base buffer action: The weak base, B, accepts protons supplied by strong acid.
The conjugate acid, BH^+, of the weak base transfers protons to the OH^- ions supplied by a strong base.

A buffer is a mixture of weak conjugate acids and bases that stabilize the pH of a solution by providing a source or sink for protons.

Sample Buffer Problem: Suppose 1.00 mol of HCOOH and 0.500 mol of NaHCOO are added to water and diluted to 1.0 L. Calculate the pH. ($K_a = 1.77 \times 10^{-4}$)

	$HCOOH + H_2O \rightleftharpoons$	H_3O^+	$+ HCOO^-$
initial molarity	1.00	0	0.500
change in molarity	-x	+x	+x
equilibrium molarity	1.00 -x	+x	0.500 + x

$K_a = 1.77 \times 10^{-4} =$

Using approximation that x is small compared to 1.00 and 0.500, x=

Check assumption

pH =

Now - what if 0.100 mol of a strong acid (HCl) had been included in the 1.0 L solution.
Because 0.100 mol of HCl reacts with equal number of moles of $HCOO^-$ to form equal moles of HCOOH:
For $HCOO^-$, 0.500 mol - 0.100 mol = 0.400 mol $[HCOO^-] = 0.400$ mol/1.0 L =0.400 M
For HCOOH, 1.00 mol + 0.100 mol = 1.10 mol [HCOOH] = 1.10 mol/1.0 L =1.10 M

$$HCOOH + H_2O \rightleftharpoons H_3O^+ + HCOO^-$$

initial molarity
change in molarity
equilibrium molarity

$K_a = 1.77 \times 10^{-4}$=

Using approximation that x is small compared to 1.10 and 0.40, x=

Check assumption (5% rule)

pH = 3.31

So addition of 0.10 mol of strong acid only changed pH from 3.45 to 3.31

Designing a Buffer

One must consider the relationship between the ratio of [HA] to $[A^-]$, the pK_a, and the desired pH.

$$HA\ (aq) + H_2O \rightleftharpoons H_3O^+\ (aq) + A^-\ (aq) \qquad K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

Rearrange: $$[H_3O^+] = K_a \times \frac{[HA]}{[A^-]}$$

Take logarithms of both sides: $$\log\ [H_3O^+] = \log\ K_a + \log\ \frac{[HA]}{[A^-]}$$

Multiply by (-) : $$-\log\ [H_3O^+] = -\log\ K_a - \log\ \frac{[HA]}{[A^-]}$$

That is: $$pH = pK_a - \log \left(\frac{[HA]}{[A^-]} \right)_{eq}$$

The values of [HA] and $[A^-]$ in the equation are at equilibrium. However, a weak acid HA typically loses only a tiny fraction of its protons, so [HA] is negligibly different from the molarity of the acid

used to prepare the buffer. Likewise, only a tiny fraction of the weakly basic anions of A^- accept protons, so $[A^-]$ is negligibly different from the molarity of A^- used to prepare the buffer.

$$\text{So} \quad pH \cong pK_a - \log \left(\frac{[HA]_0}{[A^-]_0} \right) \qquad \text{Henderson-Hasselbalch Equation}$$

initial

This assumption is valid when $[H_3O^+]$ is small compared to [HA] and $[A^-]$ (i.e. less than 5%).

Example: Design a buffer system with pH 4.60.
A buffer solution is most effective in the range of pK_a ±1
Acetic acid is suitable with a pK_a of 4.75

$$pH = pK_a - \log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0}$$

$$\log \frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = pK_a - pH = 4.75 - 4.60 = 0.15$$

$$\frac{[CH_3COOH]_0}{[CH_3COO^-]_0} = 10^{0.15} = 1.4$$

The ratio is more important than the amounts used. However, the amounts used do affect the capacity of the buffer to resist changes in pH. Higher concentrations = more resistance to change.

If you use too low concentrations, the Henderson-Hasselbalch equation won't be valid.
For pH 4.60, $[H_3O^+]$ is 2.5×10^{-5}.

$$\frac{2.5 \times 10^{-5}}{[HA] \text{ or } [A^-]} \times 100\% < 5\%$$

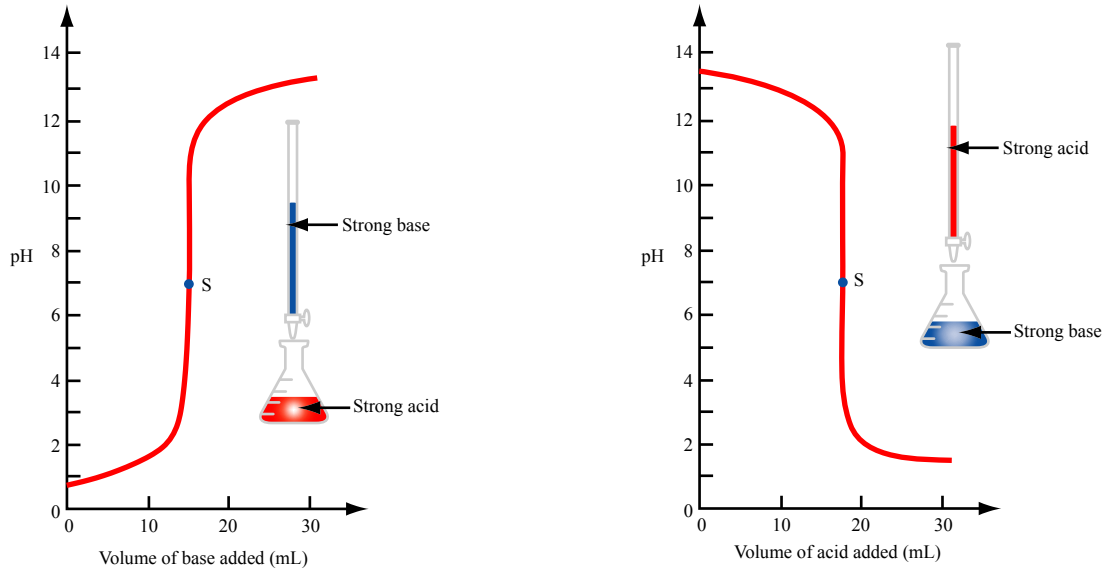
[HA] and [A-] need to be > 5.0×10^{-4} M

Today's material

Acid Base Titrations
An acid-base titration is the addition of a volume of base of known concentration to acid of unknown concentration (or addition of acid to base). This technique can be used to determine the concentration of an acid or base.

Titrations involving a strong acid and a strong base
In a titration of a strong acid with a strong base, or a strong base with a strong acid, the pH changes slowly initially, changes rapidly through pH 7 at the equivalence point and then changes slowly again.

Titration curves:



Figures by MIT OpenCourseWare.

Equivalence (stoichiometric, S) point = the theoretical volume at which the amount of base added equals the amount of acid that was originally present.

End point = the experimentally measured volume at which the indicator changes color.

Endpoint should equal equivalence point.

<u>Calculating points on a pH curve.</u>
<u>Example: a strong base (0.250 M NaOH) is titrated with a strong acid (0.340 M HCl)</u>

<u>1. Calculating the pH before the equivalence point when 5.00 mL of 0.340 M HCl (aq) is added to 25.00 mL of 0.250 M NaOH (aq)</u>

A). Calculate moles of OH^- present. (Base is strong so amount of NaOH added = amount of OH^- formed.)
0.02500 L x 0.250 mol/L = 6.25 x 10^{-3} moles

B). Calculate moles of H_3O^+ supplied by titrant. (Acid is strong so HCl added = H_3O^+ formed.)

0.00500 L x 0.340 mol/L = 1.70 x 10^{-3} moles

C). Find the moles of OH^- remaining after the reaction with H_3O^+ ions.

because stoichiometry is 1:1

6.25 x 10^{-3} moles - 1.70 x 10^{-3} moles = 4.55 x 10^{-3} mol of OH^- left

D). Calculate molarity of OH^-

4.55 x 10^{-3} mol/ 0.03000 L = 0.152 mol/L (Make sure to use total volume 5.00 mL + 25.00 mL)

E). Calculate pH

pOH = -log 0.152 = 0.818 pH = 14.00 -0.818 = 13.18

2. Calculating the volume of HCl needed to reach the equivalence point.

Initially 6.25 x 10^{-3} mol of OH^- were present. At the equivalence point, 6.25 x 10^{-3} mol of HCl will have been added (1:1 stoichiometry)

$$6.25 \times 10^{-3} \text{ mol} \times \frac{1\text{L}}{0.340 \text{ mol}} = 0.0184 \text{ L}$$

What is the pH at the equivalence point?

3. Calculate the pH after 1.00 mL of HCl has been added after equivalence point has been reached.

A). Find moles of H_3O^+ formed due to the 1.00 mL addition of HCl

(H_3O^+ formed = amount of HCl added, since strong acid)

0.340 mol/L x (0.00100 L) = 3.40 x 10^{-4} mol of H_3O^+

B). Calculate molarity of H_3O^+

C). pH = -log (7.66 x 10^{-3}) = 2.116

Titrations Curves for Weak acid/Strong base and for Weak base/Strong acid

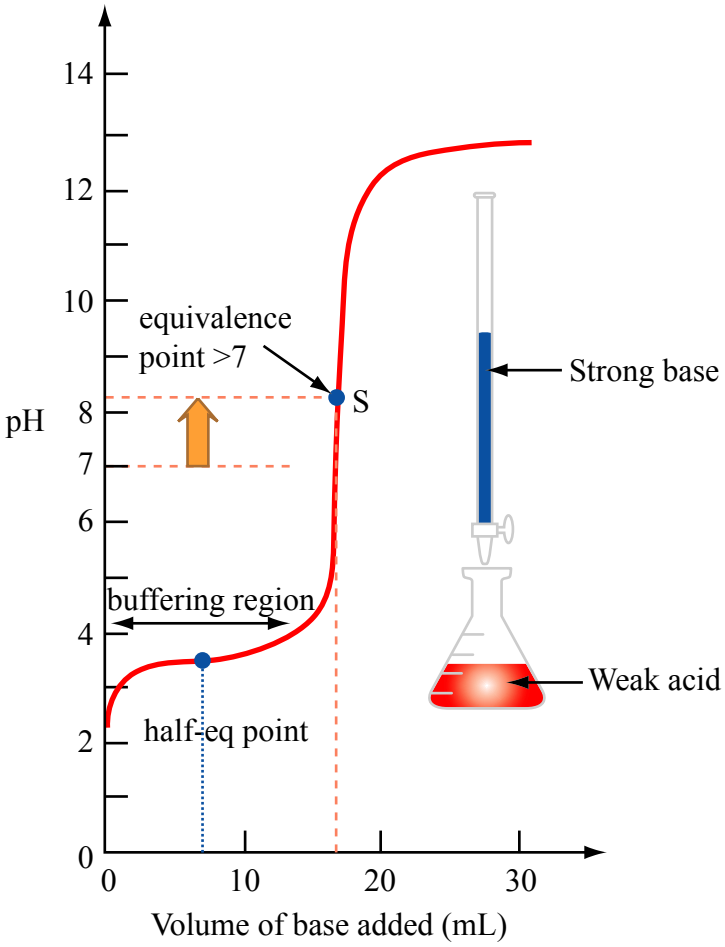
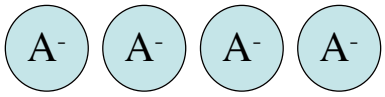


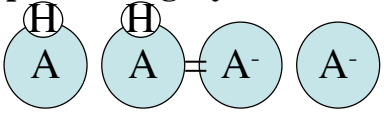
Figure by MIT OpenCourseWare.

$V > V_{eq}$ **strong base in water**

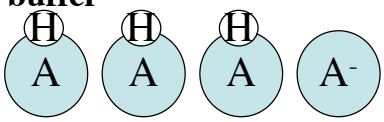
$V = V_{eq}$ **(salt) conj. base of weak acid**



$V=V_{half\text{-}eq}$ **special category of buffer**

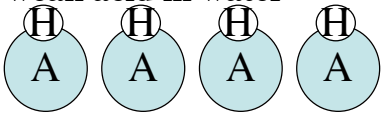


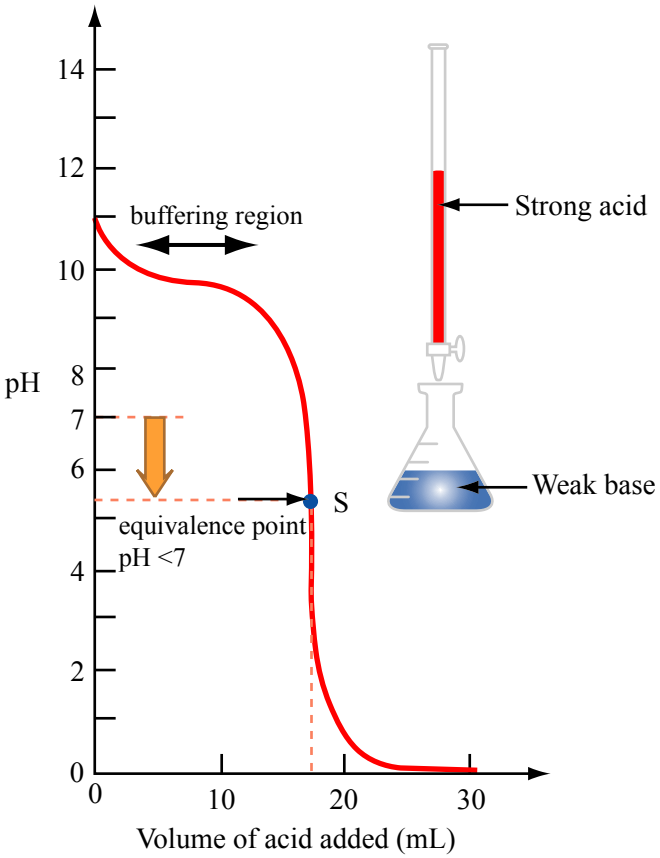
$0 < V < V_{eq}$ **buffer**



Start **weak acid in water**

V = 0





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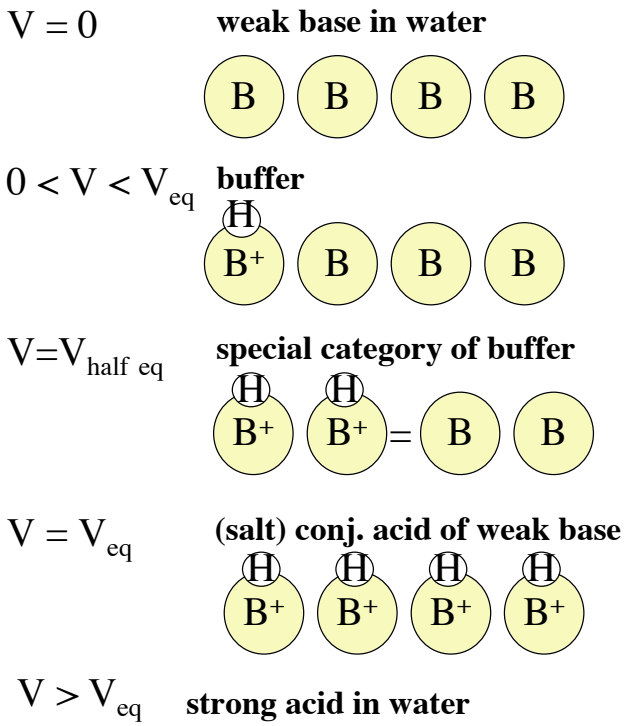

Example: Titration of weak acid with strong base
25.0 mL of 0.10 M HCOOH with 0.15 M NaOH (K_a = 1.77 x 10^{-4} for HCOOH)

1. Volume = 0 mL of NaOH added
Before any NaOH is added, the problem is that of an ionization of a weak acid in water.

$HCOOH\ (aq) + H_2O\ (l) \rightleftharpoons H_3O^+\ (aq) + HCO_2^-\ (aq)$

	HCOOH (aq)	H_3O^+ (aq) +	HCO_2^- (aq)
initial molarity	0.10 M	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.10-x	x	x

$K_a = 1.77 \times 10^{-4} = (x)^2/(0.10-x) \sim= (x)^2/0.10$

x = 0.00421 (check 0.00421 is 4.2% of 0.10) okay

pH = -log [0.00421] = 2.38 (to how many sig figs?)

2. $0 < V < V_{eq}$
In this range, the acid has been partly ionized by the strong base (buffering region).

Calculate the pH of the solution resulting from the addition of 5.0 mL of 0.15 M NaOH.
Because OH^- is a stronger base than HCO_2^-, it reacts almost completely with HCOOH.
$HCOOH\ (aq) + OH^-\ (aq) \rightarrow H_2O\ (l) + HCO_2^-\ (aq)$ K>>1

Initial Moles

For HCOOH, (25.0 x 10^{-3} L)(0.10M) = 2.5 x 10^{-3} moles

For OH^-, (5.0 x 10^{-3} L)(0.15M) = 0.75 x 10^{-3} moles

Moles after Reaction

2.5 x 10^{-3} moles - 0.75 x 10^{-3} moles = 1.75 x 10^{-3} moles of HCOOH left

0.75 x 10^{-3} moles OH^- produces 0.75 x 10^{-3} moles of HCO_2^-

Molarity

1.75 x 10^{-3} moles of HCOOH/ (0.0250 + 0.0050 L) = 0.0583 M HCOOH

0.75 x 10^{-3} moles of HCO_2^- / (0.0250 + 0.0050 L) = 0.0250 M HCO_2^-

Option 1

	HCOOH	H_3O^+ +	HCO_2^-
initial molarity	0.0583	0	0.0250
change in molarity	-x	+x	+x
equilibrium molarity	0.0583 -x	+x	0.0250 + x

K_a = 1.77 x 10^{-4} = $\frac{(0.0250 + x)(x)}{(0.0583-x)}$ assume x is small ~= $\frac{0.0250x}{0.0583}$

x = 4.13 x 10^{-4}

Check assumption: 4.13 x 10^{-4} is 1.65% of 0.025 and is 0.7% of 0.0583 okay

pH = -log [4.13 x 10^{-4}] = 3.38

Option 2

pH ~= pK_a - log ([HA]/[A^-])

pH ~= 3.75 - log ([0.0583]/[0.0250]) = 3.75 - 0.368 = 3.38

check assumption: for a pH of 3.38, [H_3O^+] = 4.2 x 10^{-4} and that is <5% of 0.0583 and is <5% of 0.0250. Okay

If the 5% assumption is not valid, than option 1 must be used and

K_a = 1.77 x 10^{-4} = (0.0250 + x)(x)/(0.0583 - x) can not be simplified.

Must solve by quadratic equation.

Note: when the volume of NaOH added is between 0 and the equivalence volume V_{eq}, the problems are similar to buffer problems. This region of the titration curve is called the "buffering region."

Half-equivalence point
When the volume of NaOH added is equal to half the equivalence volume, [HA] = [A^-].

pH ~= pK_a - log ([HA]/[A^-])
pH ~=pKa -log (1)
pH ~=pKa

3. $V = V_{eq}$
At the equivalence point, the amount of NaOH added is equal to the amount of HCOOH. The pH is not 7 as it is for a strong acid and a strong base. The pH is >7 when a weak acid is titrated with a strong base. The pH depends on the properties of the salt formed during the neutralization process. HCOOH and NaOH form $NaHCO_2$ and H_2O. Na^+ has no effect on pH and HCO_2^- is a base. Thus at the equivalence point, the pH is >7.

Calculate the pH at the equivalence point

Calculate total volume at equivalence point
moles of HCOOH = 2.5×10^{-3} moles = moles of HCO_2^- formed = moles of OH^- added

2.5×10^{-3} moles of OH^- x $\frac{1\text{L}}{0.15\text{ mol}}$ = 1.67×10^{-2} L of NaOH added
Total volume = 0.0250 L + 0.0167 L = 0.0417 L

Molarity of HCO_2^-
2.5×10^{-3} moles of HCO_2^-/ (0.0417 L) = 0.0600 M HCO_2^-

This is an ionization of weak base in water problem.

HCO_2^- (aq) + H_2O (l) $\rightleftharpoons$ HCOOH (aq) + OH^- (aq)

	HCO_2^- (aq)	HCOOH (aq) + OH^- (aq)	
initial molarity	0.0600	0	0
change in molarity	-x	+x	+x
equilibrium molarity	0.0600 -x	+x	+ x

You can take it from here. Simplify if x is small compared to 0.0600 M. Calculate x, which is equal to [OH^-] = 1.83×10^{-6} M. Then calculate pOH = 5.74. From pOH, calculate pH.
pH = 8.26 (which is >7)

4. $V > V_{eq}$

Beyond the equivalence point, NaOH is added to the solution of the conj. base HCO_2^-. Since HCO_2^- does not give rise to much OH^- in solution (1.83×10^{-6} M), the pOH and pH are determined by the amount of excess NaOH added. This problem is similar to a strong acid/strong base problem.

At 5.00 mL past the equivalence point:

0.00500 L x 0.15 M = 7.5×10^{-4} moles excess OH^-

7.5×10^{-4} moles OH^- /(0.00500 L + 0.0250 L+ 0.0167 L) = 0.016 M OH^-

pOH = -log [0.16] = 1.79

pH = 12.21