Lecture 4a

Last time:

Equivalence point calculations

buffers

Today:

calculations using buffer equation

pH titration curve

Field trip to LA COUNTY SANITATION WATER DISTRICT

WHEN: July 27, 2009 - Monday

TIME: 2:15-3:30 pm-visit treatment plant

WHERE: 1965 So. Workman Mill Road, Whittier, CA

(closest exit: Crossroads at 60 Fwy, just east of 605 Fwy)

WHAT: Visit San Juan Creek Water Quality Laboratory.

EXTRA CREDIT? Yes. 15-25 points

Pls. sign up if you are interested.

Buffer equation

Known as the Henderson-Hasselbalch equation, the buffer equation is used to approximate the pH of a buffer.

Once you master it, it is a quick way to determine pH

It will come in handy in determining the pH titration curve.

Deriving the buffer equation

Start off with Ka equilibrium: $HA <==> H^+ + A^-$

$K_a = [H^+] [A^-] / [HA]$

Take the - log of both sides and rearrange:

$-\log K_a = -\log[H^+] - \log \{[A^-]/[HA]\}$ recognize pK_a and pH ?

$pH = pK_a + \log \{[A^-]/[HA]\}$

Generally: the Henderson-Hasselbalch eq. is written:

$$pH = pK_a + \log \{[base]/[acid]\}$$

Applying the HH equation: Example 1

[acid]≥[base]

Suppose a solution is made up of 0.200 M acetic acid HAc, and 0.100M sodium acetate (NaAc). This is a buffer right?

What are the conjugate acids and bases?

$K_a = 1.8 \times 10^{-5}$ for HAc. So $pK_a = -\log(1.8 \times 10^{-5}) = 4.74$

$$pH = pK_a + \log \{[base]/[acid]\}$$

$pH = 4.74 + \log (0.100M/0.200M) = 4.74 - 0.30 = 4.44$

Take home message: $pH < pK_a$ when [acid]>[base]

Applying the HH equation: Example 2

Equal concs.

Suppose a solution is made up of 0.200 M acetic acid HAc, and 0.200M sodium acetate (NaAc). (note: $pK_a = 4.74$)

$$pH = pK_a + \log \{[base]/[acid]\}$$

$pH = 4.74 + \log (0.200M/0.200M) = 4.74 + 0.00 = 4.74$

Take home message: when the [base] = [acid], the $pH = pK_a$

As we will see, a buffer is most effective in resisting pH change when it is within ±1 pH unit of its pK_a

Applying the HH equation: Example 3

[base]>[acid]

Suppose a solution is made up of 0.100 M acetic acid HAc, and 0.200M sodium acetate (NaAc). (note: $pK_a = 4.74$)

pH = pK$_a$ + log {[base]/[acid]}

pH = 4.74 + log (0.200M/0.100M) = 4.74 + 0.30 = 5.04

Take home message: when the [base] > [acid], the pH>pK$_a$

Titration

Titrant

Analyte

4 regions in a pH titration of a weak acid or weak base.

1) V=0, 2) $0<V<V_{ep}$

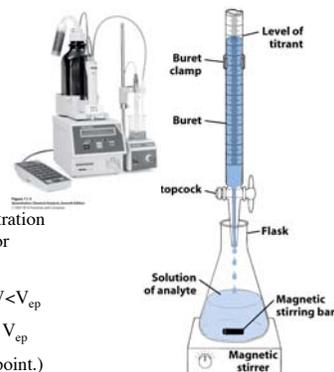3) $V = V_{ep}$; 4) $V > V_{ep}$

(note: "V_{ep} " = eq point.)

Weak acid vs strong base: 4 regions of pH titration curve:

Region I: No base is added. Solution is "pure weak acid". pH is determined by K_a equilibrium.

Region II: buffer region: weak acid and conjugate base present. Use buffer equation.

Region III: equivalence point: Solution is "pure weak base". pH determined using K_b equilibrium.

Region IV: after equiv. Pt: Solution is "strong base" solution. pH is obtained by first determining pOH of the strong base.

Example 4: Titration of weak acid with strong base:

Example: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence point.

Determine the pH of the solution at various points of the titration:

a) V_{NaOH} =0   b) V_{NaOH} = 5.00 mLs,   c) V_{NaOH} = 12.5 mLs

d) V_{NaOH} = 20.0 mLs; e) V_{NaOH} = 25.00 mLs; f) 30.0mLs

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

We need [HAc]$_o$ (initial): Use $M_{HAc}V_{HAc} = M_{OH}V_e$

M_{HAc} = (0.100M)(25.0mL)/(25.0mL)=0.100M

a) At V_{OH} = 0.00mLs, we use the K_a equilibrium:

HAc < = = > H$^+$ + Ac$^-$ K_a =[H$^+$][Ac$^-$] /[HAc]
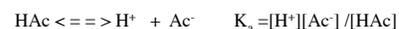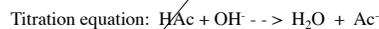
0.100-x   x   x K_a = x^2/(0.100-x) =>

$1.8 \times 10^{-5} \approx x^2/(0.100)$ by 5% rule; solve for x (=[H$^+$])

[H$^+$] = x = 1.3×10^{-3} => pH = -log(1.3×10^{-3}) =2.87

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

mmol HAc = MV = (25.0mL)(0.100M)=2.50 mmol, etc

b) V_{OH} = 5.0 mL : Use **pH = pK$_a$ + log {[base]/[acid]}**

Titration equation: HAc + OH$^-$ - - > H$_2$O + Ac$^-$

I	2.5mmol	+0.5mmol	0
C	-0.5mmol	-0.5mmol	+0.5mmol
E	2.0mmol	0	0.5mmol

So [Ac$^-$] = 0.50mmol/(25.0+5.0)=0.0167M

[HAc] = 2.0mmol/(25.0+5.0)=0.0667 M

pH = 4.74 + log(.0167/0.0667) = 4.14 (notice that it's rising)

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

b) V_{OH} = 5.0 mL : Use **pH = pK_a + log {[base]/[acid]}**

Let's repeat it with a "short cut". Since we know V_e =25.0mL,

25.0 mLs

can let 25.0mLs represent initial moles of HAc. 5.0mLs represents moles HAc reacted (converted to Ac⁻) so 25-5 represents HAc unreacted. (still HAc).

5.0=Ac⁻	25.0-5.0 = HAc

So [Base]/[acid] = V_{OH} / (V_e-V_{OH}) = 5/(25-5)=0.25

pH = 4.74 + log(5/20) = 4.74 -.60= 4.14 (same as before)

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

c) V_{OH}=12.5 mls (= 1/2 V_{ep}) : Still buffer region,

Here,

Ac⁻=12.5	HAc=25-12.5=12.5

Moles HAc = moles Ac⁻

So, pH = 4.74 + log (12.5/12.5) =4.74 + log(1) = 4.74+0 = 4.74

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

d) V_{OH}=20.0 mls : Still buffer region,

Here,

20.0	5.0

So, pH = 4.74 + log (20.0/5.0) =4.74 + log(4) = 4.74+.60 = 5.34

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

e) V_{OH}=25.0 mls (= V_{ep}) : Solution is pure weak base.

Use K_b equilibrium: Ac⁻ + H_2O < = = > HAc + OH⁻

$\qquad\qquad$ 0.0500-x $\qquad\qquad$ x $\qquad$ x

Here, [Ac⁻]= 100M(25.0mL/(25.0+25.0)mL = 0.0500M

x^2/(0.0500-x) = K_b =K_w/K_a =$10^{-14.00}$/$10^{-4.74}$ = 5.5x10^{-10}

x^2≈ (0.0500)(5.5x10^{-10}) => x=[OH⁻] = 5.2x10^{-6}=> pOH=5.28

So, pH = 14.00-5.28 =8.72 (still rising)

Example 4: A 25.0 mL HAc solution is titrated with 0.100 M NaOH standard, requiring 25.0 mLs to reach equivalence pt.

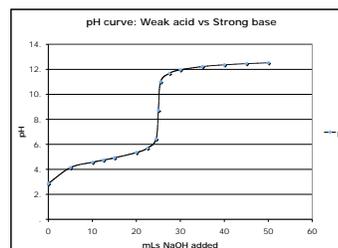f) V_{OH}=30.0 mls (> V_{ep}) : Solution is pure strong base.

Here, need pOH = -log[NaOH]$_{excess}$

So: [OH⁻]$_{excess}$ = M_{OH}(V_{OH}–V_{ep}) / (V_{OH} + V_{HAc})

$\qquad$ =(0.100M)(30.0-25.0)/(25.0+30.0) = 0.0091

pOH = 2.04 ; pH = 14.00-2.04 = 11.96

Master this process! For the midterm.

Practice drawing pH titration curves.

pH curve: Weak acid vs Strong base

Graphing the pH curve:

It's important to recognize the various regions of the graph. And how to draw it with minimum of points.

Figure 11-2
Quantitative Chemical Analysis, Seventh Edition
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pH curve for strong acids vs strong bases has no Ka buffering region

Figure 11-1
Quantitative Chemical Analysis, Seventh Edition
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pH indicators: phenolphthalein (Phph)

pH indicators : example phenolphthalein is a weak acid

HPhph $<===>$ H$^+$ + Phph$^-$
colorless   pink-red

At its pK$_a$ it changes color. If its pK$_a$ is at the center of the equivalence point inflection, then it is ideally suited for the titration…

Figure 11-9
Quantitative Chemical Analysis, Seventh Edition
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You draw it for the following:

a) weak base (analyte) vs Strong acid (titrant)

b) Strong acid (analyte) vs strong base (titrant)

c) Strong base (analyte) vs strong acid (titrant)

On Wednesday: we discuss
titration curve of diprotic weak acid vs strong base
K$_{sp}$ and K$_f$