Video
1703
(5:17)

Buffers, Titrations, and Solubility Equilibria

Name: ____________________

AP Chemistry Lecture Outline

The Common-Ion Effect

For THIS 'WEAK' in soln...	$CH_3COOH \rightleftharpoons CH_3COO^- + H^+$
...if we add in THIS ION...	
...by mixing in, say, THIS SALT...	
...Le Chatelier says we'd shift...	
Ionization of the 'weak' will have...	
...and the mixture will have a ___ pH than the 'weak' soln alone.	

For THIS 'WEAK' in soln..	$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^-$
...if we add in THIS ION...	
...by mixing in, say, THIS SALT...	
...Le Chatelier says we'd shift...	
Ionization of the 'weak' will have...	
...and the mixture will have a ___ pH than the 'weak' soln alone.	

For THIS 'WEAK' in soln...	$HBrO_2 \rightleftharpoons H^+ + BrO_2^-$
...if we add in THIS ION...	
...by mixing in, say, THIS SALT...	
...Le Chatelier says we'd shift...	
Ionization of the 'weak' will have...	
...and the mixture will have a ___ pH than the 'weak' soln alone.	

For THIS 'WEAK' in soln...	$HF \rightleftharpoons H^+ + F^-$
...if we add in THIS ION...	
...by mixing in, say, THIS SALT...	
...Le Chatelier says we'd shift...	
Ionization of the 'weak' will have...	
...and the mixture will have a ___ pH than the 'weak' soln alone.	

"So, what's the common-ion effect?"

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EX. Find the pH of 0.085 nitrous acid, which has a K_a of 4.5×10^{-4}.

EX. Find the pH of a mixture of 0.085 M nitrous acid and 0.10 M potassium nitrite.

Video 1709 (6:28)

Buffered Solutions ("buffers")

-- a mixture of…

-- such solutions...

e.g.,

Obviously, the common-ion effect plays a role in the operation of buffers.

"How Does a Buffer Work?"

Consider a buffer containing the 'weak' chlorous acid and the salt lithium chlorite.

Because of the 'weak', we've got plenty of... i.e.,

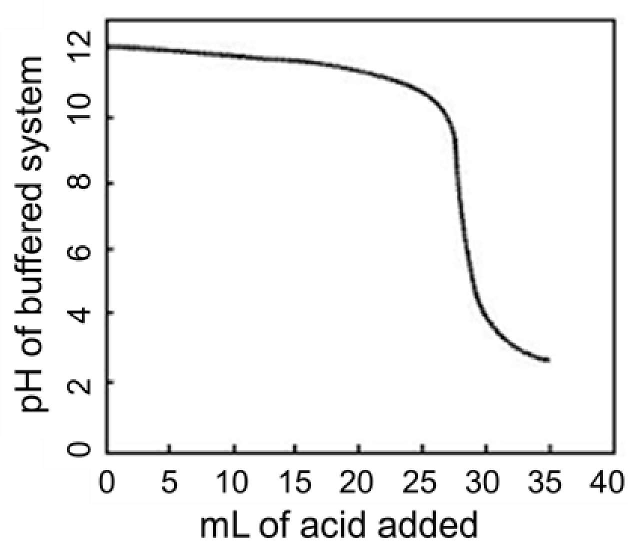
Because of the salt, we've got plenty of... i.e.,

Thus, if some strong acid is added to this buffer, the ______ will _________ protons; if some strong base is added, the ______ will _________ protons. In either case, the pH of the buffer remains relatively stable.

The amount of added strong acid or added strong base that a buffer can handle before the pH begins to change appreciably is called the buffer capacity.

-- Buffer capacity INCREASES with GREATER moles (i.e., greater ____ and ____) of both 'weak' and salt.

Ironically, while buffer capacity depends on the absolute amounts of both 'weak' and salt, the pH of a buffered system at any given time depends only on the ________ of the two.



Video 1712 (5:26)

pH of Buffered Solutions

The pH of a buffered soln depends on two factors:

(1) the ____ of the 'weak'

(2) the ______of the 'weak' and common ion [ ]s

With regard to (2)...

If ['weak'] = [common ion],

If ['weak'] > [common ion],

If ['weak'] < [common ion],

EX. Nitrous acid has K_a 7.2 x 10^{-4}. When a buffer has equal concentrations of nitrous acid and nitrite ion (from, say, sodium nitrite), find mixture's pH.

OR if $[HNO_2] > [NO_2^-]$, the pH tips toward the 'weak'.

OR if $[HNO_2] < [NO_2^-]$, the pH tips toward the ion.

Video 1715 (7:00)

There are two ways to deal with calculations involving appreciable amounts of 'weak' and salt (like in buffers):

(1)

(2)

ACID form of the H-H equation:

BASE form of the H-H equation:

EX. Find the pH of a buffer that is 0.12 M lactic acid, $HC_3H_5O_3$ (K_a = 1.4 x 10^{-4}) and 0.10 M sodium lactate.

But first, a short and quick detour. Recall that a buffer's pH (or pOH) is NEAR...

For this case, the [acid] > [ion], so we expect the pH here to be...

EX. Find the pH of a buffer that is 0.12 M lactic acid, $HC_3H_5O_3$ ($K_a = 1.4 \times 10^{-4}$) and 0.10 M sodium lactate, but this time using an H-H equation.

Video 1718 (9:32)

Addition of Strong Acids or Bases to Buffers

-- Reactions between ‘strongs’ and ‘weaks’ proceed to completion (i.e., all of the ‘strong’ is consumed).

-- When adding a ‘strong’ to either a ‘weak’ or a buffer...

(1)

(2)

EX. 2.00-L of a buffered solution of pH 4.74 contains 0.30 mol of acetic acid ($K_a = 1.8 \times 10^{-5}$) and 0.30 mol of sodium acetate. Calculate the pH after 0.040 mol of sodium hydroxide is added. Ignore volume changes.

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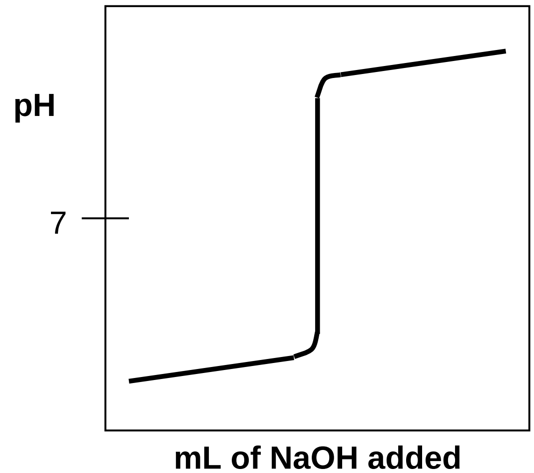
Acid-Base Titrations

<u>equivalence point</u>:

pH curve for HCl titrated with NaOH



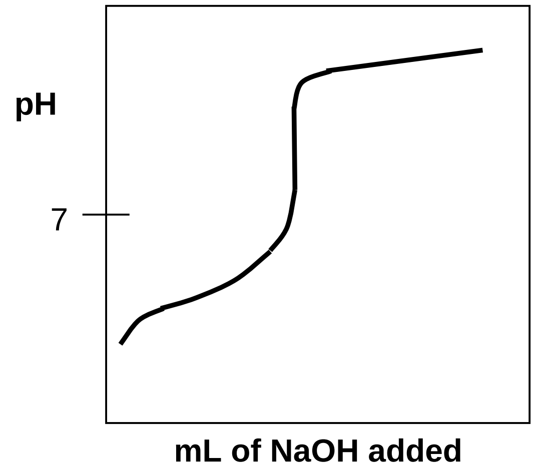
<u>Strong Acid – Strong Base Titrations</u>

Any indicator whose color change begins and ends along the vertical section of the titration curve is okay.

-- phenolphthalein (pH 8.3-10.0)

-- methyl red (pH 4.2-6.0)

pH curve for CH_3COOH titrated with NaOH



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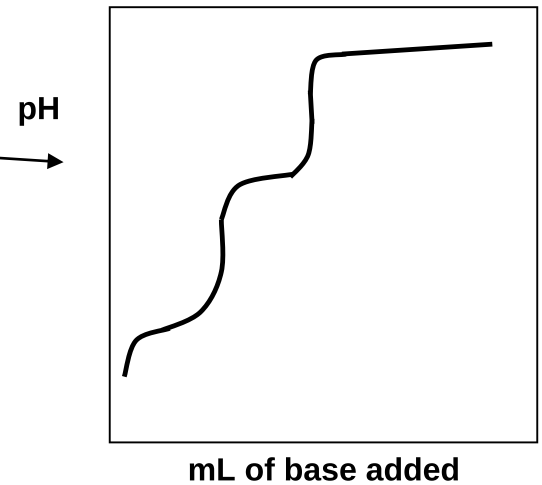
<u>Weak Acid – Strong Base Titrations</u>

The equivalence point is when, say, 50.0 mL of 0.10 M NaOH have been added to 50.0 mL of 0.10 M CH_3COOH, but pH is > 7 at that point because...

pH curve for H_2CO_3



Titration curves for <u>polyprotic acids</u> (e.g., H_2CO_3) look something like

-- they have...

EX. Calculate the pH at the equivalence point if 40.0 mL of 0.0250 M benzoic acid (C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$) are titrated with 0.050 M sodium hydroxide.

C_6H_5COOH OH^-

Video 1727 (9:01)

Mixing Non-Stoichiometric Amounts of Acid and Base

EX. Find pH when 24.90 mL of 0.10 M nitric acid are mixed with 25.00 mL of 0.10 M potassium hydroxide.

EX. Calculate the pH when 10.0 mL of 0.080 M sodium hydroxide are added to 40.0 mL of 0.0250 M benzoic acid (C_6H_5COOH, $K_a = 6.3 \times 10^{-5}$).

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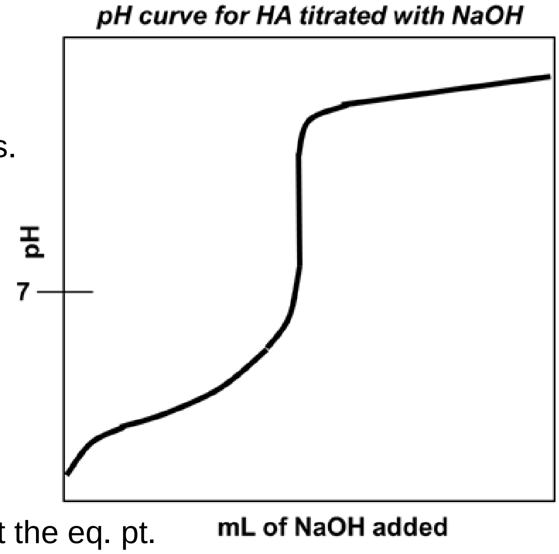
The Half-Equivalence Point for a Strong-Weak Titration

Suppose we are titrating the weak acid HA with the strong base NaOH. As we do so, we measure the pH after every mL of base added. If we graph pH vs. mL of base added, we get a plot that looks like...



At the equivalence point, the pH will be ___ 7
because the ___ produced will act as a...

We use the graph to determine the pK_a of the weak acid, and here's how...

From the graph, we determine the vol. of base added at the eq. pt.

Then we calculate HALF of this volume, and find the corresponding point on the graph.

This is the... Here, the soln's pH = __________

The math of Henderson-Hasselbalch backs this up.

Thus: During titration, we have...

At the half-eq. pt...

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Solubility Equilibria

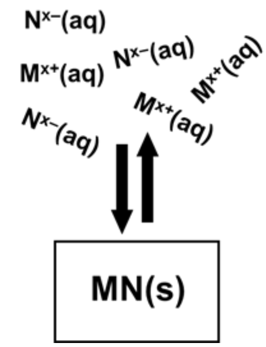
-- involve the dissolution or precipitation of "insoluble" salts, e.g.,

Consider a saturated solution of a typical 'insoluble':

For these cases, the <u>solubility-product constant K_{sp}</u> is equal to (respectively):

K_{sp} expressions NEVER have denominators because…

-- K_{sp} is the eq. constant btwn undissolved and dissolved ionic solute in a saturated aqueous soln of an 'insoluble.'



small K_{sp}...

large K_{sp}...

EX. Write the solubility-product constant expression for lead (II) chloride.

Video 1736 (7:28)

EX. Copper (II) azide has $K_{sp} = 6.3 \times 10^{-10}$. Find the solubility of $Cu(N_3)_2$ in water, in g/L.

EX. Find the solubility of zinc hydroxide ($K_{sp} = 3.0 \times 10^{-16}$) in a soln buffered at pH = 11.43.

Video 1739 (7:47)

Precipitation of Ions

For $BaSO_4(s) \rightleftharpoons Ba^{2+}(aq) + SO_4^{2-}(aq)$... $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

We could reach equilibrium from the left...

or from the right...

At any given time, the <u>ion product</u> $Q = [Ba^{2+}][SO_4^{2-}]$

If $Q > K_{sp}$...

If $Q < K_{sp}$...

If $Q = K_{sp}$...

EX. Will a precipitate form from mixing 0.10 L of 8.0×10^{-3} M lead (II) nitrate and 0.40 L of 5.0×10^{-3} M sodium sulfate?

Video 1742 (6:01)

Factors Affecting Solubility

1. As soln temp. $\uparrow$ / $\downarrow$, solubility...

--

2. adding/removing commons ions e.g. $CaF_2(s) \rightleftharpoons Ca^{2+}(aq) + 2\ F^-(aq)$

-- If we add Ca^{2+} or F^- ions (by adding, say, $CaCl_2$ or NaF powder), system shifts...

-- Similarly, if we somehow remove either Ca^{2+} or F^- ions, system shifts...

3. The solubility of some compounds – most notably, ones that have anions that act as bases – is affected by pH changes. Consider the compound $Fe(OH)_2$.

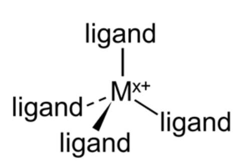
If we acidify the soln, $[OH^-]$...
...and the solubility of $Fe(OH)_2$...

If we somehow increase the pH, $[OH^-]$...
...and the solubility of $Fe(OH)_2$...

Other anions besides OH^- that would behave similarly are...

Video 1745 (9:36)

4. In the presence of specific Lewis bases, the solubility of ‘insolubles‘ is affected if the metal in the ‘insoluble’ forms a <u>complex ion</u> with those Lewis bases.



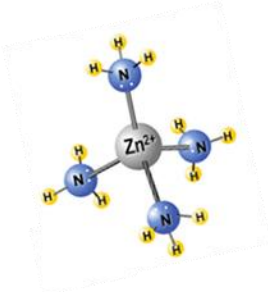
Typical Lewis bases that become ligands (i.e., are IN complex ions):

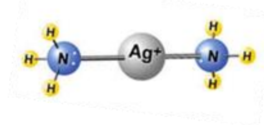
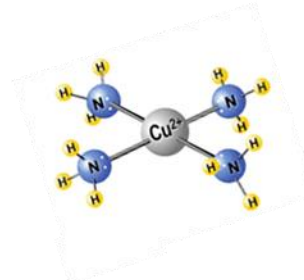
The number of ligands that surround the metal ion is called the...

The three most common coord. #s are...

Complex ions have geometries that we've met before...

Several complex ions:	$Ag(CN)_2^-$	$Cd(NH_3)_4^{2+}$	$Co(NH_3)_6^{3+}$
	$Ag(NH_3)_2^+$	$CuCl_4^{2-}$	$Fe(H_2O)_6^{3+}$
	$Al(OH)_4^-$	$Cu(CN)_4^{2-}$	$Zn(NH_3)_4^{2+}$
	$Cd(CN)_4^{2-}$	$Cu(NH_3)_4^{2+}$	$Zn(OH)_4^{2-}$



e.g., In a soln of AgCl, we have the equilibrium:

AgCl in soln (lots of AgCl(s))

after adding sufficient NH_3 (lots of $Ag(NH_3)_2^+$(aq))

If ammonia is added, we get…

The solubility of 'insolubles' __ in the presence of any Lewis base that the 'insoluble's' metal forms a complex ion with.

Video 1748 (8:29)

Selective Precipitation and Qualitative Analysis

<u>selective precipitation</u>: using the different solubilities of ions to separate them

Say we want to separate the Ag^+ and Cu^{2+} in a soln that contains both. First, let's add plenty of HCl...

$CuCl_2$ is...

AgCl is…

-- Separate the insoluble _____ from the soluble _____ by...

Qualitative Analysis for Metallic Elements

-- determines the presence or absence of a particular ion

--

Steps:

(1)

(2)