

Topics:

Common Ion Effect
From Salts and Partial Neutralization

Buffer Systems: Resisting Changes in pH
The Henderson-Hasselbalch Equation

Acid-Base Titrations
Titration Curves of Strong and Weak Acids & Bases
Titration Curves of Polyprotic Acids

Indicators: Endpoint vs. Equivalence Point

Solubility Product of Slightly Soluble Salts (K_{sp})
Common Ion Effect

Precipitation Reactions Revisited

Solubility and Complex ions

Solubility, Ion Separations, and Qualitative Analysis

The Common Ion Effect:

The ionization of an acid or base is limited by the presence of its conjugate base or acid (based on Le Chatelier's Principle)

Can occur from:

- The effect of a partial neutralization of an acid or base
- The presence of a salt containing the conjugate of the acid or base

Affects the equilibrium expression of the acid or the base.

Example 1:

What is the pH of the solution that results from adding 30.0mL of 0.100M NaOH to 45.0mL of 0.100M acetic acid?

Moles NaOH: $(.0300L)(0.100M) = .0030\text{mol NaOH}$
Moles $\text{HC}_2\text{H}_3\text{O}_2$: $(.0450L)(0.100M) = .0045\text{ HC}_2\text{H}_3\text{O}_2$
.0030mol of the acid are neutralized leaving:
.0030mol $\text{C}_2\text{H}_3\text{O}_2^-$ (.04M) and .0015mol $\text{HC}_2\text{H}_3\text{O}_2$ (.02M)
 K_a for acetic acid is 1.8×10^{-5}
 $1.8 \times 10^{-5} = (x)(.04+x) / (.02-x)$
 $x = 8.99 \times 10^{-6} = [\text{H}_3\text{O}^+]$ $\text{pH} = -\log(8.99 \times 10^{-6}) = 5.05$
*Note that since x is small, the equation can be simplified to $1.8 \times 10^{-5} = (x)(.04/.02)$ and you get almost the same answer.

Example 2:

Assume you have a 0.30M solution of formic acid (HCO_2H) and have added enough sodium formate (NaHCO_2) to make the solution 0.10M in the salt. Calculate the pH of the formic acid solution before and after adding sodium formate.

Answer:

pH before:
 $1.8 \times 10^{-4} = (x)(x) / (0.30 - x)$ $x = 7.26 \times 10^{-3}$
 $\text{pH} = -\log(7.26 \times 10^{-3}) = 2.139 = 2.14$

pH after:
 $1.8 \times 10^{-4} = (x)(x+0.10) / (0.30-x)$ $x = 5.36 \times 10^{-4}$
 $\text{pH} = -\log(5.36 \times 10^{-4}) = 3.27$

Buffer Systems

Resists changes to pH when a strong acid or base is added

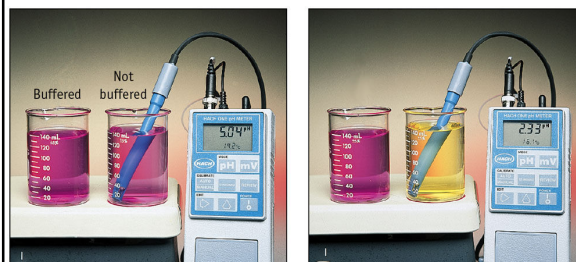
Requirements:

- An acid capable of scavenging added OH^- ions and a base capable of scavenging added H_3O^+ ions.
- The acid and the base of the buffer must not react with each other

Made from weak acids and salts of their conjugate bases or weak bases and salts of their conjugate acids

Relies on the common ion effect

5mL of 0.10M HCl added to buffered and nonbuffered systems (containing bromphenol blue indicator). Note the lack of color change for the buffered system



Buffers and the Henderson-Hasselbalch Equation

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

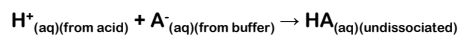
$$[H_3O^+] = \frac{K_a[HA]}{[A^-]}$$

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

Henderson-Hasselbalch Equation

How Buffer Systems Work

For added strong acid:



For added strong base:



The best range of pH buffering occurs when the desired pH (to be buffered) is very close to the pK_a of the weak acid being used in the buffer system

Buffers with sufficient molarity must be used so as not to "exhaust" the buffer.

Example:

Using an acetic acid/sodium acetate buffer solution, what ratio of acid to conjugate base will you need to maintain the pH at 5.00? (K_a for acetic acid is 1.8×10^{-5})

Answer:

$$5.00 = 4.74 + \log(\text{acetate ion} / \text{acetic acid})$$

$$.26 = \log(\text{acetate ion} / \text{acetic acid})$$

$$(\text{acetate ion} / \text{acetic acid}) = 10^{.26} = 1.82$$

So you would need a **1.82:1** mol (molarity) ratio of acetate to acetic acid

Example:

Calculate the pH of 0.500L of a buffer solution composed of 0.50M formic acid (HCO_2H) ($K_a = 1.8 \times 10^{-4}$) and 0.70M sodium formate ($NaHCO_2$) before and after adding 10.0mL of 1.0M HCl

Answer:

Before: $pH = -\log(1.8 \times 10^{-4}) + \log(0.70/0.50)$
= 3.89

After:

Molarity formic: $[0.50M(0.500L) + 1.0M(0.0100L)]/0.510L = .5098M$
 Molarity formate: $[0.70M(0.500L) - 1.0M(0.0100L)]/0.510L = .6667M$

$$pH = -\log(1.8 \times 10^{-4}) + \log(.6667/.5098) = \mathbf{3.86}$$

Acid-Base Titrations

Titration: Quantitatively determining the concentration of a solution by reacting it with another solution of precisely known concentration.

Terminology

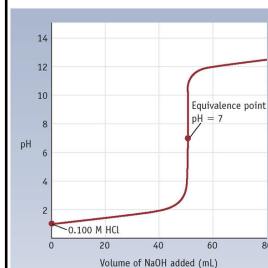
Titrant: The solution of known concentration used to titrate a volume of the solution of unknown concentration.

Standardized (standard) solution: Solution of precisely known concentration

Equivalence point: The point at which stoichiometrically equivalent amounts of reactants have reacted

Endpoint: The point where an indicator (such as pH) changes color.

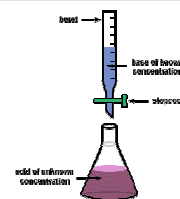
Strong Acid – Strong Base Titration Curve



50.0 mL of 0.100 M HCl titrated with 0.100 M NaOH

Volume of base added, mL	pH
100.0	12.52
80.0	12.36
60.0	11.96
50.0	11.68
51.0	11.00
50.0	7.00
49.0	3.00
48.0	2.69
45.0	2.28
40.0	1.95
20.0	1.37
10.0	1.18
0.0	1.00

very large amount 13.00 (maximum)



The pH at the equivalence point of a strong acid-strong base titration is 7.

The pH of the equivalence point is taken as the mid-point in the vertical portion of the pH versus volume of titrant curve.

Example:

What is the pH after 25.0mL of 0.100M NaOH has been added to 50.0mL of 0.100M HCl? What is the pH after 50.50mL of NaOH has been added?

Answer

mol acid left: $(0.0500\text{L})(0.100\text{M}) - (0.0250\text{L})(0.100\text{M}) = .0025\text{mol}$

New $[\text{H}_3\text{O}^+] = .0025\text{mol}/.075\text{L} = .033\text{M}$

$\text{pH} = -\log(.033) = 1.48$

At 50.50mL of NaOH all of the HCl is neutralized and an extra 0.50mL of .100M NaOH exists in solution.

$[\text{OH}^-] = (0.0005\text{L})(0.100\text{M}) / .10050\text{L} = 4.975 \times 10^{-4}$

$\text{pOH} = -\log(4.975 \times 10^{-4}) = 3.303$

$\text{pH} = 14.0 - 3.303 = 10.7$

Titration of a Weak Acid with a Strong Base

The pH before the titration begins is given by the equilibrium expression using K_a of the weak acid

The pH at the equivalence point is dominated by the conjugate base (in the salt that forms) from the weak acid that was titrated.

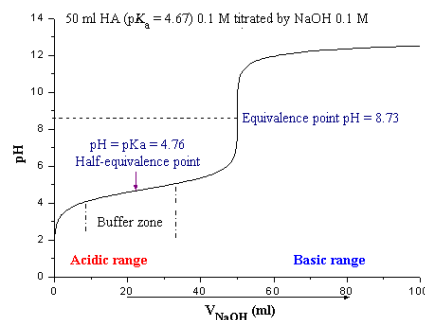
The pH at the halfway point (half-equivalence point) is given by:

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

at the halfway point $[\text{A}^-] = [\text{HA}]$ and the $\log(1) = 0$ therefore

$$\text{pH} = \text{p}K_a$$

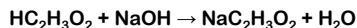
Note that the pH at the equivalence point will be greater than 7 (see titration curve below)



Example:

What is the pH of the solution when 35.0mL of 0.100M NaOH has been added to 100.0mL of 0.100M acetic acid?

Answer:



Moles NaOH = $(.0350\text{L})(0.100\text{M}) = .0035\text{ mol}$

Moles $\text{HC}_2\text{H}_3\text{O}_2 = (.1000\text{L})(0.100\text{M}) = .0100\text{ mol}$

$$\text{pH} = \text{p}K_a + \log\left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}\right)$$

since moles and molarity are related here (same solution volume)

$$\text{pH} = 4.74 + \log(.0035\text{mol} / (.0100 - .0035)) = 4.47$$

Random Review Problem:

A student wishes to produce 600.mL of a buffer system that is .500M in nitrous acid ($K_a = 6.0 \times 10^{-4}$) and buffers at a pH of 3.00. To make the solution, the student will be using 1.00M stock nitrous acid solution and solid potassium nitrite (85.10g/mol)

- Calculate the volume of stock nitrous acid that should be used.
- Calculate the mass of potassium nitrite that should be used.
- Outline a method for producing the final 600.mL of buffer solution.

Answer:

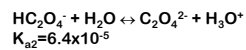
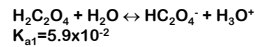
a) 600.mL of buffer that is .500M in HNO_2 is desired.
Using the dilutions equation $M_1V_1 = M_2V_2$
 $(.500\text{M})(600.\text{mL}) = (1.00\text{M})(V_2)$
 $V_2 = 300.\text{mL}$ of stock 1.00M solution should be used

b) $\text{pH} = \text{pK}_a + \log\left(\frac{[\text{NO}_2^-]}{[\text{HNO}_2]}\right)$
 $3.00 = 3.22 + \log(x / .500\text{M})$
 $x = .603 (.500\text{M}) = .301\text{M}$ in potassium nitrite
 $\text{mol KNO}_2 = (.301\text{M})(.600\text{L}) = .181\text{mol}$
 $\text{g KNO}_2 = (.181\text{mol})(85.10\text{g/mol}) = 15.383 = 15.4\text{g KNO}_2$

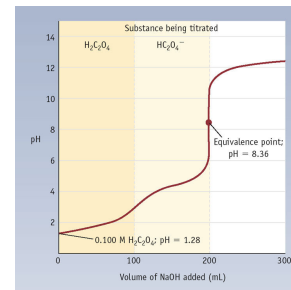
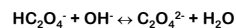
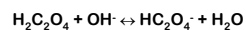
c) Method: Measure out 300.mL of 1.00M nitrous acid.
Add 15.4g KNO_2 . Dilute with water to 600.mL

Titration of a Weak Polyprotic Acid with a Strong Base

Dissociation of the weak acid, oxalic acid:



Titration with .100M NaOH:

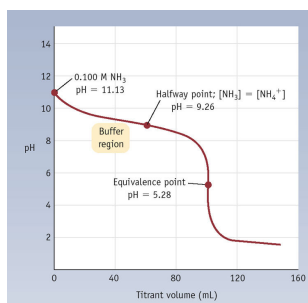


Note that the base properties of the oxalate ion, $\text{C}_2\text{O}_4^{2-}$ makes the solution basic at the equivalence point.

Titration of a weak base with a Strong Acid

pH at the midpoint of the titration = pK_a of the conjugate acid of the weak base.

The pH is somewhat acidic at the equivalence point



Example:

Calculate the pH after 75.0mL of 0.100M HCl has been added to 100.0mL of 0.100M NH_3 (K_b of $\text{NH}_3 = 1.8 \times 10^{-5}$)

Answer:

$\text{mol HCl} = (.0750\text{L})(0.100\text{M}) = .00750\text{mol HCl}$

initial moles $\text{NH}_3 = (.100\text{L})(0.100\text{M}) = .0100\text{mol NH}_3$

Final:

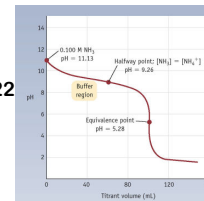
$\text{mol NH}_4^+ = .00750\text{mol}$

$\text{mol NH}_3 = .0100 - .00750 = .0025\text{mol}$

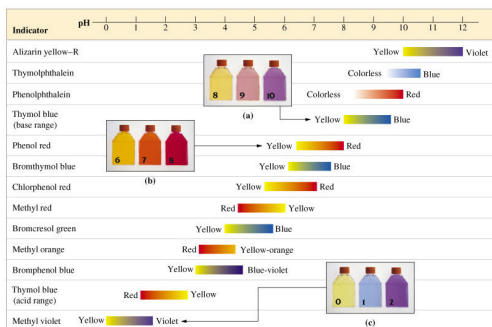
$\text{pOH} = \text{pK}_b + \log\left(\frac{[\text{NH}_4^+]}{[\text{NH}_3]}\right)$

$\text{pOH} = 4.74 + \log(.00750/.0025) = 5.22$

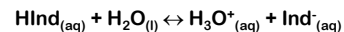
$\text{pH} = 14.00 - 5.22 = 8.78$



Acid-Base Indicators



Substances (usually weak organic acids or bases) that change color at different pH levels. Useful for identifying specific pH values in solution.



$$[\text{H}_3\text{O}^+] = \frac{[\text{HInd}]}{[\text{Ind}^-]} + K_a$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{Ind}^-]}{[\text{HInd}]}\right)$$

The indicator does not change the experiment since only a drop or two are used

Color changes can generally only be observed when:

Color of HInd when $[\text{HInd}]/[\text{Ind}^-]$ is 10/1

Color of Ind^- when $[\text{HInd}]/[\text{Ind}^-]$ is 1/10

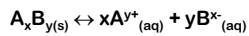
Example:

Use the list on slide 23 to determine the best indicator to use for the titration on slide 21 (titrating a weak base with a strong acid.)

Answer: Methyl red has an endpoint closest to the equivalence point.

Solubility of Salts

For a given slightly soluble salt of the form:



$$K_{sp} = [A^{y+}]^x[B^{x-}]^y$$

Where K_{sp} is the solubility product constant (equilibrium constant) for the salt (in aqueous solution)

Can be used to determine solubility (in mol/L or g/100mL H₂O, etc.)

Example:

Knowing that the K_{sp} value for MgF_2 is 5.2×10^{-11} , calculate the solubility of the salt in a) moles per liter and b) grams per liter

Answer:

$$5.2 \times 10^{-11} = [X][2X]^2$$

$$X = 2.35 \times 10^{-4} = 2.4 \times 10^{-4} \text{ mol/L}$$

$$2.4 \times 10^{-4} \text{ mol/L} (62.3 \text{ g/mol}) = 0.015 \text{ g MgF}_2/\text{L}$$

Direct comparisons of the solubility of two salts on the basis of their K_{sp} values can only be made for salts having the same cation to anion ratio.

Ex. $Ca(OH)_2$ solubility is based on

$$K_{sp} = [Ca^{2+}][OH^-]^2 \text{ whereas}$$

$CaSO_4$ solubility is based on

$$K_{sp} = [Ca^{2+}][SO_4^{2-}]$$

To determine relative solubility in this case, X must be solved for.

Solubility and the Common Ion Effect

The effect of having an ion already in solution that is common to one of the ions in a substance being added to the solution (with a given K_{sp}) is to reduce the solubility of that substance.

Example:

Calculate the solubility of $BaSO_4$ a) in pure water and b) in the presence of 0.010M $Ba(NO_3)_2$. K_{sp} for $BaSO_4$ is 1.1×10^{-10} .

Answer:

a. $K_{sp} = [Ba^{2+}][SO_4^{2-}]$

$$1.1 \times 10^{-10} = (x)(x)$$

$$x = 1.0 \times 10^{-5} \text{ mol/L}$$

b. $1.1 \times 10^{-10} = (x+0.010)(x)$

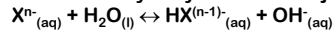
$$x = 1.1 \times 10^{-8} \text{ mol/L}$$

The Effect of Basic anions on Salt Solubility

Any salt containing an anion that is the conjugate base of a weak acid will dissolve in water to a greater extent than given by K_{sp}

Why?

Because of hydrolysis of the conjugate base given by:

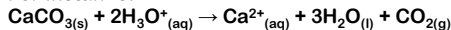


(Salts containing phosphate, acetate, carbonate, cyanide and sulfide salts, etc.)

Modified solubility products that take this fact into account are given by K_{spa} ($= K_{sp}K_b$) values (see margin p882)

Insoluble salts in which the anion is the conjugate base of a weak acid dissolve in strong acids. Conjugates of strong acids do not.

For Instance:



K_{sp} and the Reaction Quotient, Q

Recall that Q gives the current state of the system relative to equilibrium (in this case K_{sp})

$Q = K_{sp}$: solution is saturated and at equilibrium

$Q < K_{sp}$: solution is not saturated

$Q > K_{sp}$: solution is supersaturated

By changing concentrations, Q can be adjusted

Examples:

1. Solid PbI_2 ($K_{sp} = 9.8 \times 10^{-9}$) is placed in a beaker of water. After a period of time, the lead(II) concentration is measured and found to be $1.1 \times 10^{-3}\text{M}$. Has the system reached equilibrium (saturated)? If not, will more PbI_2 dissolve?

2. Will SrSO_4 precipitate from a solution containing $2.5 \times 10^{-4}\text{M}$ strontium ion, Sr^{2+} , if enough of the soluble salt Na_2SO_4 is added to make the solution $2.5 \times 10^{-4}\text{M}$ in SO_4^{2-} ? (K_{sp} for SrSO_4 is 3.4×10^{-7})

3. What is the minimum concentration of I^- that can cause precipitation of PbI_2 from a 0.050M solution of $\text{Pb}(\text{NO}_3)_2$? K_{sp} for PbI_2 is 9.8×10^{-9} . What concentration of Pb^{2+} ions remains in solution when the concentration of I^- is 0.0015M ?

Answers:

1. $Q = (1.1 \times 10^{-3})(2.2 \times 10^{-3})^2 = 5.3 \times 10^{-9}$

This is less than K_{sp} (9.8×10^{-9}) so **more PbI_2 will dissolve.**

2. $Q = (2.5 \times 10^{-4})(2.5 \times 10^{-4}) = 6.3 \times 10^{-8}$

This is smaller than K_{sp} (3.4×10^{-7}) so it will **not precipitate**

3. $9.8 \times 10^{-9} = (0.050\text{M})(X)^2$

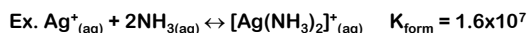
$X = 4.4 \times 10^{-5} = [\text{I}^-]$

$9.8 \times 10^{-9} = (X)(.0015\text{M})^2$

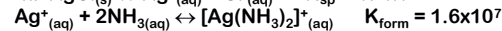
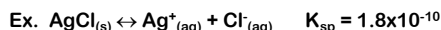
$X = 4.4 \times 10^{-3}\text{M} = [\text{Pb}^{2+}]$

Solubility and Complex Ions

The degree to which a metal ion forms a complex in solution is given by the formation constant K_{form}



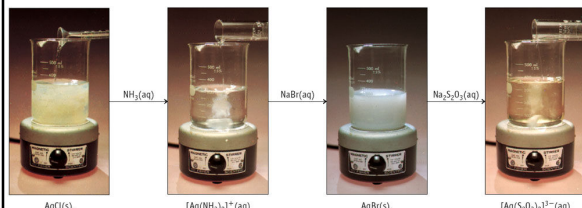
This can affect how much of a slightly soluble compound dissolves in solution.



$K_{net} = K_{sp} \times K_{form} = (1.8 \times 10^{-10})(1.6 \times 10^7) = 2.9 \times 10^{-3}$

$2.9 \times 10^{-3} = [\text{Ag}(\text{NH}_3)_2^+][\text{Cl}^-]/[\text{NH}_3]^2$

Using Equilibrium Constants to Control a Reaction



$\text{AgCl}_{(s)}$
 $K_{sp} = 1.8 \times 10^{-10}$

Aqueous silver nitrate to which sodium chloride has been added

$[\text{Ag}(\text{NH}_3)_2]^+_{(aq)}$

Addition of ammonia to drive complex formation

$K_{form} = 1.6 \times 10^7$

$\text{AgBr}_{(s)}$
 $K_{sp} = 5.4 \times 10^{-13}$

Addition of sodium bromide to form stable AgBr

$[\text{Ag}(\text{S}_2\text{O}_3)_2]^{3-}_{(aq)}$

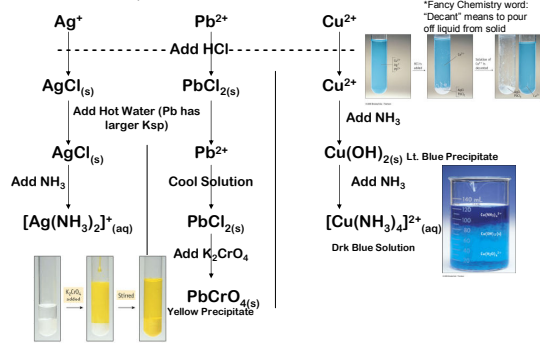
Addition of sodium thiosulfate to form thiosulfate complex

$K_{form} = 2.0 \times 10^{13}$

Remember: Low K_{sp} values favor undissociated compounds. High K_{form} values favor complex formation.

Solubility, Ion Separations and Qualitative Analysis

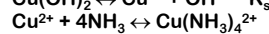
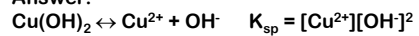
Separation and ID of Ions in Solution



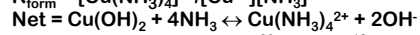
Example:

Calculate the value of the equilibrium constant, K_{net} , for dissolving $\text{Cu}(\text{OH})_2$ in aqueous ammonia to form the complex ion $[\text{Cu}(\text{NH}_3)_4]^{2+}$. K_{sp} for $\text{Cu}(\text{OH})_2$ is 2.2×10^{-20} (appendix j) and K_{form} for $[\text{Cu}(\text{NH}_3)_4]^{2+}$ is 6.8×10^{12} (appendix k)

Answer:



$$K_{\text{form}} = \frac{[\text{Cu}(\text{NH}_3)_4]^{2+}}{[\text{Cu}^{2+}][\text{NH}_3]^4}$$



$$K_{\text{net}} = K_{\text{sp}} \times K_{\text{form}} = (2.2 \times 10^{-20})(6.8 \times 10^{12})$$

$$= 1.5 \times 10^{-7}$$