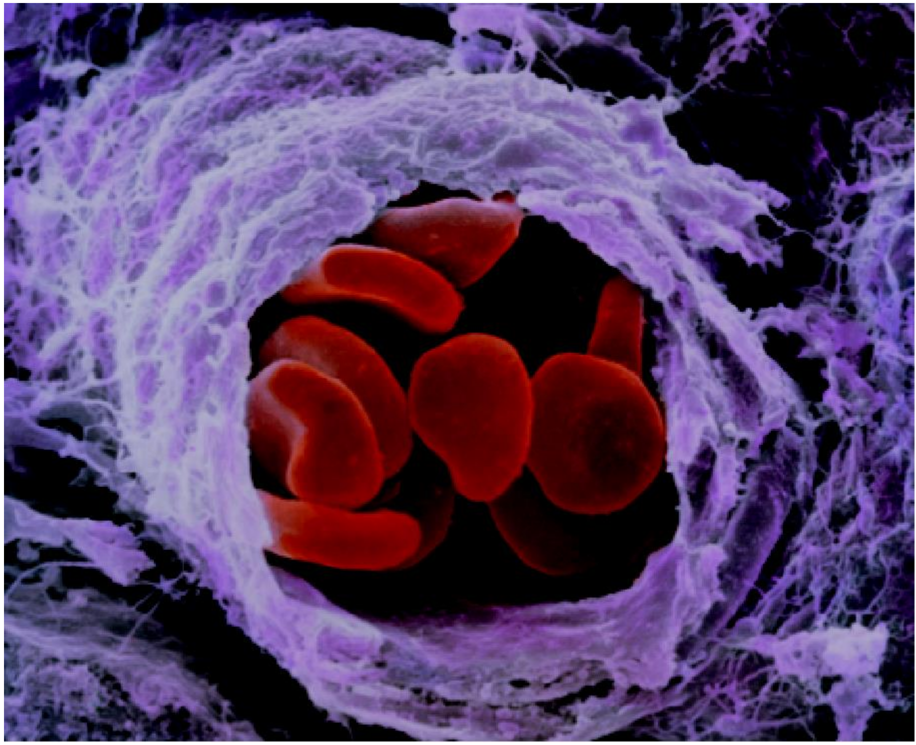
Acid-Base and Solubility Equilibria



Acid-Base Theories

i) The Arrhenius Theory of acids and bases

- ✓ Acids are substances which produce hydrogen/hydronium ions in solution, example HCl.
- ✓ Bases are substances which produce hydroxide ions in solution, example NaOH.

ii) The Bronsted-Lowry Theory of acids and bases

- ✓ An acid is a proton (hydrogen ion) donor, example CH_3COOH.
- ✓ A base is a proton (hydrogen ion) acceptor, example H_2O.

iii) The Lewis Theory of acids and bases

- ✓ An acid is an electron pair acceptor, example BF_3.
- ✓ A base is an electron pair donor, example NH_3.

The ***common ion effect*** is the shift in equilibrium caused by the addition of a compound having an ion in common with the dissolved substance.

The presence of a common ion **suppresses** the ionization of a weak acid or a weak base.

Consider mixture of CH_3COONa (strong electrolyte) and CH_3COOH (weak acid).

$$CH_3COONa\,(s) \longrightarrow Na^+\,(aq) + \boxed{CH_3COO^-\,(aq)}$$

$$CH_3COOH\,(aq) \rightleftharpoons H^+\,(aq) + \boxed{CH_3COO^-\,(aq)}$$

$$\longleftarrow$$

common ion

Consider mixture of salt NaA and weak acid HA.

$$\mathrm{NaA}\ (s) \longrightarrow \mathrm{Na}^+\ (aq) + \mathrm{A}^-\ (aq)$$

$$\mathrm{HA}\ (aq) \rightleftarrows \mathrm{H}^+\ (aq) + \mathrm{A}^-\ (aq)$$

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

$$[\mathrm{H}^+] = \frac{K_a\,[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$-\log\,[\mathrm{H}^+] = -\log K_a - \log \frac{[\mathrm{HA}]}{[\mathrm{A}^-]}$$

$$-\log\,[\mathrm{H}^+] = -\log K_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]}$$

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\mathrm{A}^-]}{[\mathrm{HA}]} \qquad \mathrm{p}K_a = -\log K_a$$

Henderson-Hasselbalch equation

$$\mathrm{pH} = \mathrm{p}K_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

What is the pH of a solution containing 0.30 *M* HCOOH and 0.52 *M* HCOOK?

Mixture of weak acid and conjugate base!

$$HCOOH\ (aq) \rightleftharpoons H^+\ (aq) + HCOO^-\ (aq)$$

	$HCOOH\ (aq)$	$H^+\ (aq)$	$HCOO^-\ (aq)$
Initial (*M*)	0.30	0.00	0.52
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.30 - x$	x	$0.52 + x$

Common ion effect

$0.30 - x \approx 0.30$

$0.52 + x \approx 0.52$

HCOOH pK_a = 3.77

$$pH = pK_a + \log \frac{[HCOO^-]}{[HCOOH]}$$

$$pH = 3.77 + \log \frac{[0.52]}{[0.30]} = 4.01$$

A ***buffer solution*** is a solution of:

1. A weak acid or a weak base **and**
2. The salt of the weak acid or weak base

Both must be present!

A buffer solution has the ability to resist changes in pH upon the addition of small amounts of either acid or base.

Consider an equal molar mixture of CH_3COOH and CH_3COONa

Add strong acid

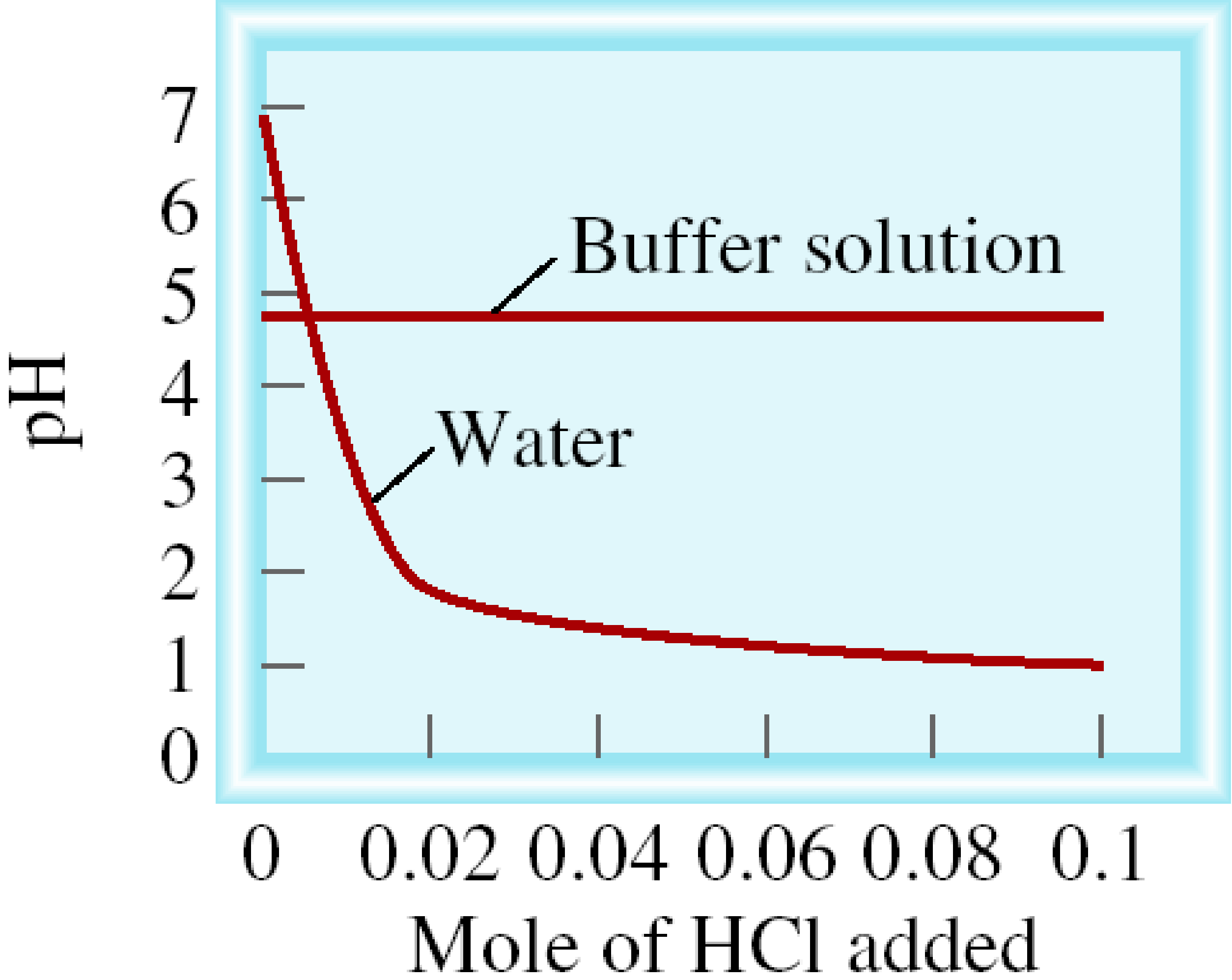
$$H^+ \,(aq) + CH_3COO^- \,(aq) \longrightarrow CH_3COOH \,(aq)$$

Add strong base

$$OH^- \,(aq) + CH_3COOH \,(aq) \longrightarrow CH_3COO^- \,(aq) + H_2O \,(l)$$

$$HCl \longrightarrow H^+ + Cl^-$$

$$HCl + CH_3COO^- \longrightarrow CH_3COOH + Cl^-$$



Which of the following are buffer systems?

(a) KF/HF

(b) KBr/HBr

(c) $Na_2CO_3/NaHCO_3$

(a) HF is a weak acid and F^- is its conjugate base

buffer solution

(b) HBr is a strong acid

not a buffer solution

(c) CO_3^{2-} is a weak base and HCO_3^- is its conjugate acid

buffer solution

Calculate the pH of the 0.30 *M* NH_3/0.36 *M* NH_4Cl buffer system. What is the pH after the addition of 20.0 mL of 0.050 *M* NaOH to 80.0 mL of the buffer solution?

$$NH_4^+\ (aq) \rightleftharpoons H^+\ (aq) + NH_3\ (aq)$$

$$pH = pK_a + \log\frac{[NH_3]}{[NH_4^+]} \qquad pK_a = 9.25 \qquad pH = 9.25 + \log\frac{[0.30]}{[0.36]} = \boxed{9.17}$$

start (moles) 0.029 0.001 0.024

$$NH_4^+\ (aq) + OH^-\ (aq) \longrightarrow H_2O\ (l) + NH_3\ (aq)$$

end (moles) 0.028 0.0 0.025

final volume = 80.0 mL + 20.0 mL = 100 mL

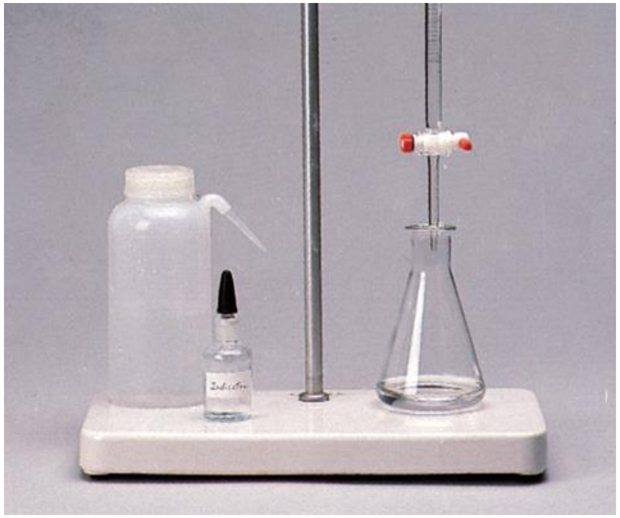
$$[NH_4^+] = \frac{0.028}{0.10} \qquad [NH_3] = \frac{0.025}{0.10} \qquad pH = 9.25 + \log\frac{[0.25]}{[0.28]} = \boxed{9.20}$$

Titration

In a titration a solution of accurately known concentration is added gradually to another solution of unknown concentration until the chemical reaction between the two solutions is complete.

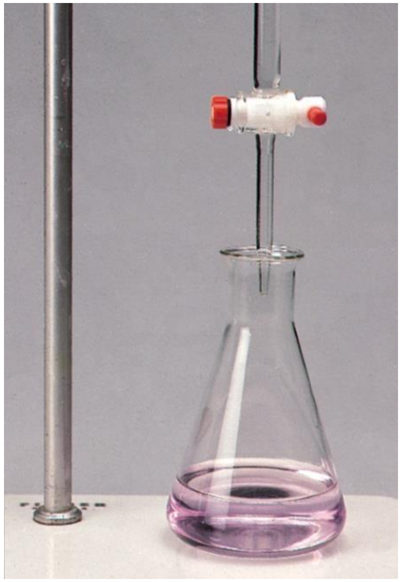
Equivalence point – the point at which the reaction is complete

Indicator – substance that changes color at (or near) the equivalence point



Slowly add base to unknown acid UNTIL

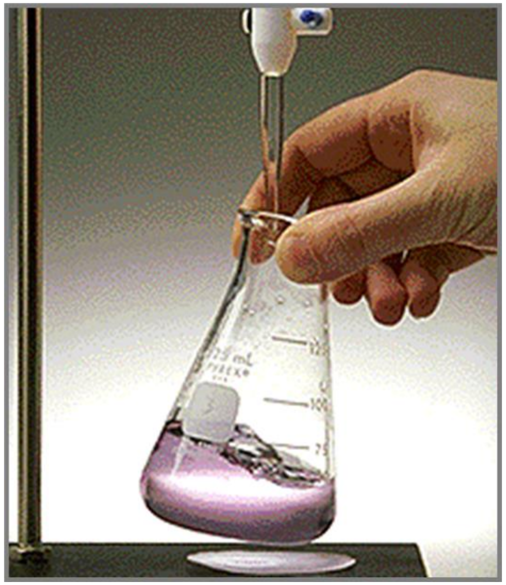
The indicator changes color (pink)



Titration-cont……

- Analytical method in which a standard solution is used to determine the concentration of an unknown solution.

Known solution concentration

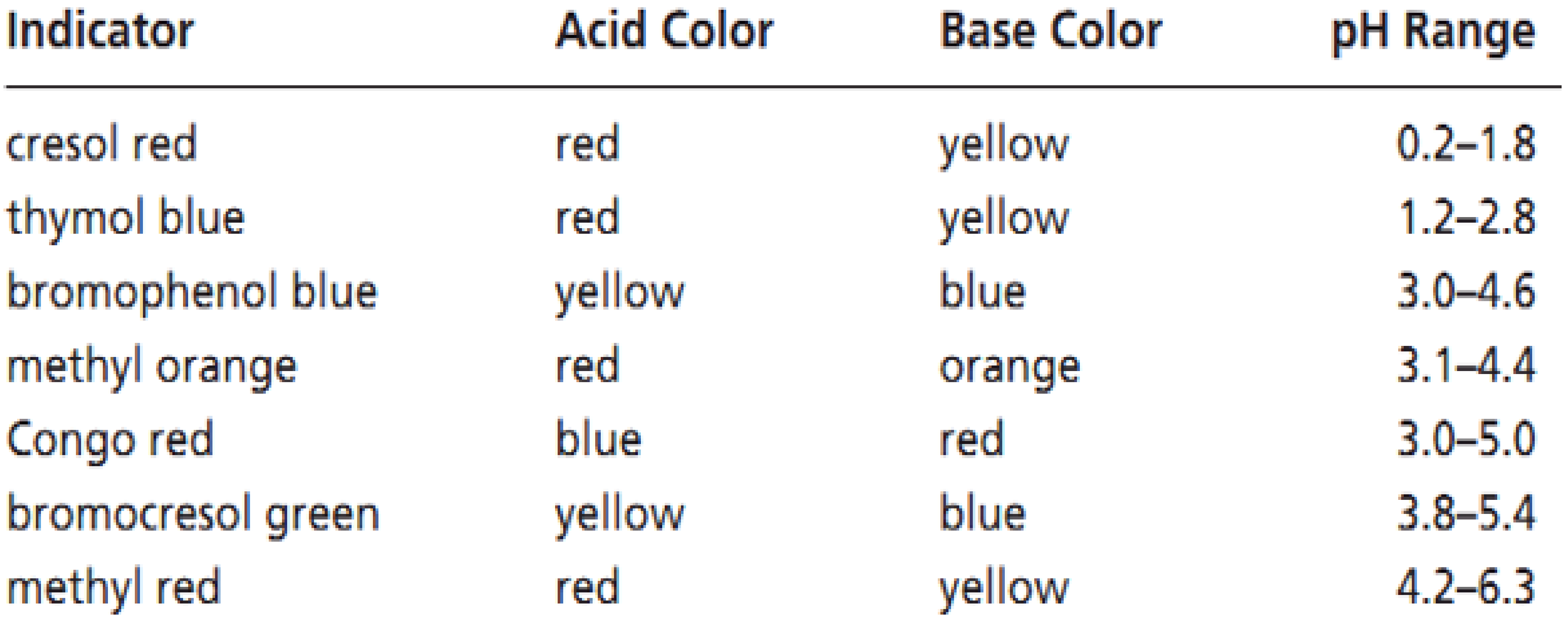


Unknown solution concentration

- Titration is the process of adding a standard solution to a solution of analyte until the reaction between the analyte and the reagent is judged to be complete.
- Laboratory method for determining the concentration of an analyte

Acid-base indicators

They are weak acid/weak base whose ionized form is a different color than its undissociated form.



Indicator	Acid Color	Base Color	pH Range
cresol red	red	yellow	0.2–1.8
thymol blue	red	yellow	1.2–2.8
bromophenol blue	yellow	blue	3.0–4.6
methyl orange	red	orange	3.1–4.4
Congo red	blue	red	3.0–5.0
bromocresol green	yellow	blue	3.8–5.4
methyl red	red	yellow	4.2–6.3

bromocresol purple	yellow	purple	5.2–6.8
litmus	red	blue	5.0–8.0
bromothymol blue	yellow	blue	6.0–7.6
phenol red	yellow	red	6.8–8.4
cresol red	yellow	red	7.2–8.8
thymol blue	yellow	blue	8.0–9.6
phenolphthalein	colorless	red	8.3–10.0
alizarin yellow R	yellow	orange/red	10.1–12.0

In titration, the solution of accurately known concentration i.e.; standard solution is called the **Titrant** and the substance to be determined is called **Titrand or analyte.**

The point in a titration at which the amount of titrant added is chemically equivalent to the amount of substance titrated i. e. The point at which the completion of the reaction occurs is called the **equivalence point** or **theoretical** or **stoichiometric end point**.

The point at which the completion of a reaction is practically observed is called **end point.**

Strong Acid-Strong Base Titrations

- Acid-Base titration is based on the titration of bases by a standard acid (acidimetry) or titration of acids by a standard base (alkalimetry).
- Acid-Base titration is also known as a neutralization titration which is widely used to determine the amounts of acids and bases
- The standard reagents used in acid/base titrations are always strong acids or strong bases, most commonly HCl, HClO4, H2SO4, NaOH, and KOH.
- Weak acids and bases are never used as standard reagents because they react incompletely with analytes

❖ In the titration of a:-

- strong acid -strong base, the salt is neutral, pH at equivalence point = 7

- strong acid and weak base, the salt is acidic, pH at equivalence point < 7
- strong base and weak acid, the salt is basic, pH at equivalence point > 7

Example: Consider the titration of 50.0 mL of 0.100 M HCl with 0.200 M NaOH.

Pre-equivalent point: Before any base is added the pH is directly calculated from the concentration of the acid, HCl. Initially the solution is 0.100 M in HCl, which, since HCl is a strong acid, means that the pH, pH = -log[H_3O^+] = -log[HCl] = - log(0.100) = 1.00.

- After addition of some amount of base, before the equivalence point, HCl is present in excess and the pH is determined by the concentration of excess HCl.
- For example, after adding 10.0 mL of NaOH, the concentration of excess HCl is

$$[\mathrm{HCl}] = \frac{\text{moles excess HCl}}{\text{total volume}} = \frac{M_aV_a - M_bV_b}{V_a + V_b}$$

$$[\mathrm{HCl}] = \frac{(0.100\mathrm{M})(50.0\mathrm{mL}) - (0.200\mathrm{M})(10.0\mathrm{mL})}{50.0\mathrm{mL} + 10.0\mathrm{mL}} = 0.05$$ giving a pH of 1.30.

Equivalent point

At the equivalence point the moles of HCl and the moles of NaOH are equal. Since neither the acid nor the base is in excess, the pH is determined by the dissociation of water.

$K_w = 1.00 \times 10^{-14} = [H_3O^+][OH^-]$, $1.00 \times 10^{-7} = [H_3O^+]$, Thus, the pH at the equivalence point is 7.00.

At the equivalence point moles of HCl is equal to that of moles NaOH. The volume of NaOH needed to reach the equivalence point, therefore, is calculated as from the relationship

$$M_aV_a = M_bV_b$$

$$V_{eq} = V_b = \frac{M_aV_a}{M_b} = \frac{(0.100\mathrm{mL})(50.0\mathrm{mL})}{0.200\mathrm{M}} = 25\mathrm{mL}$$

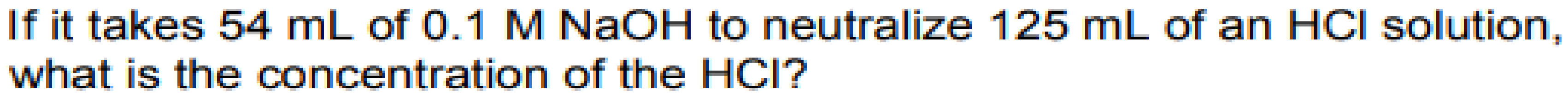
Post-Equivalent point

At this point, there is an excess of NaOH, and pH is determined by the concentration of excess OH^-. For example, after adding 30.0 mL of titrant the concentration of OH^- is

$$[\mathrm{NaOH}] = \frac{\text{moles excess NaOH}}{\text{total volume}} = \frac{M_b V_b - M_a V_a}{V_a + V_b} = \frac{(0.200\mathrm{mL})(30.0\mathrm{mL}) - (0.100\mathrm{mL})(50.0\mathrm{mL})}{50.0\mathrm{mL} + 30.0\mathrm{mL}}$$

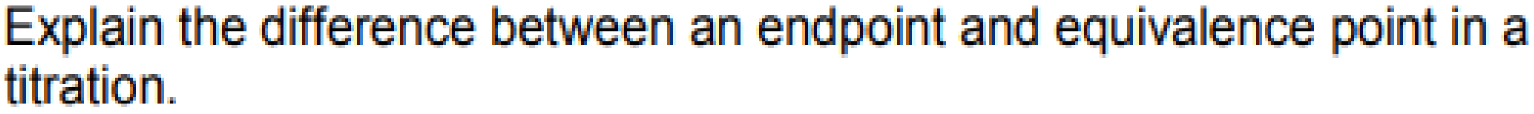
$$= 0.0125\mathrm{M}$$

What is pH after 0.0 mL, 10.0mL, at equivalence point, and 50.0 mL of base has been added during the titration of 25.0 mL of a 0.12M HCl solution with 0.15M NaOH solution?



If it takes 54 mL of 0.1 M NaOH to neutralize 125 mL of an HCl solution, what is the concentration of the HCl?

If it takes 25 mL of 0.05 M HCl to neutralize 345 mL of NaOH solution, what is the concentration of the NaOH solution?



Explain the difference between an endpoint and equivalence point in a titration.

Define the following terms

a. Analyte

b. Titrant

c. Standard Solution

d. Equivalence Point

e. End Point

f. Indicators

g. Burette

h. Volumetric Pipet

i. Erlenmeyer Flask

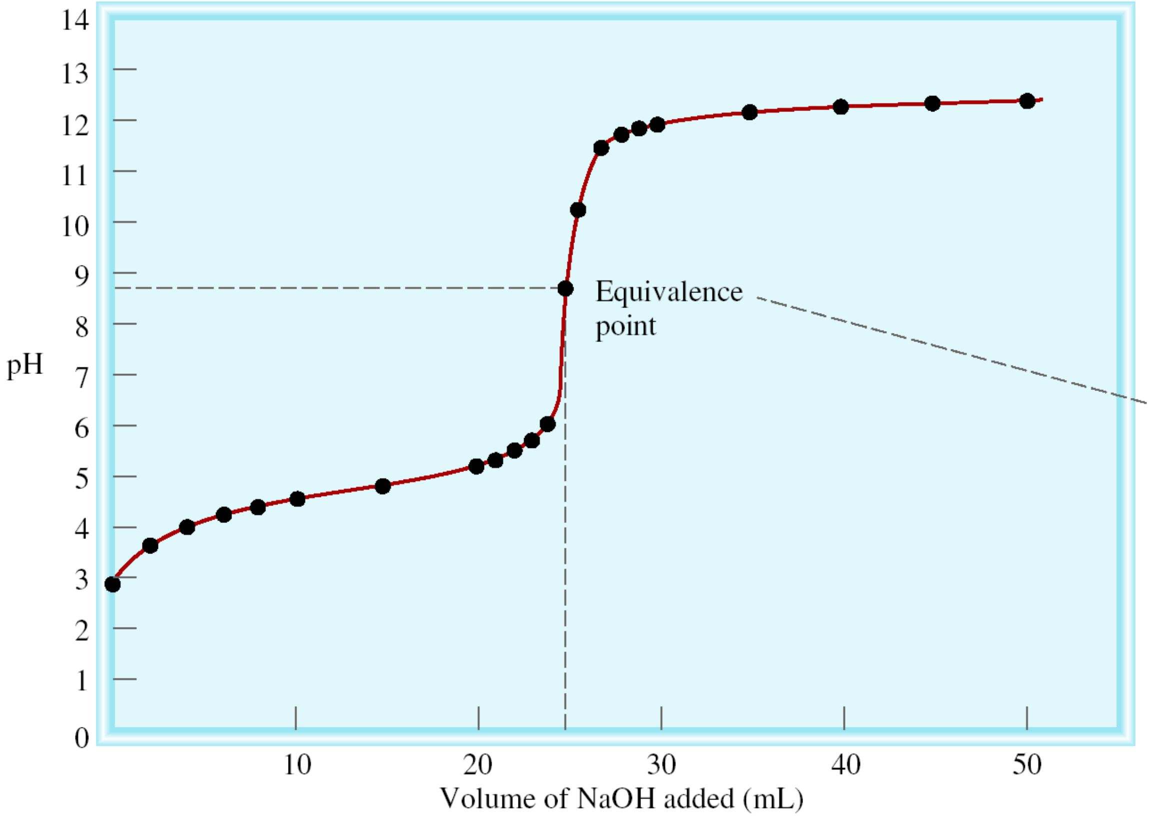
Weak Acid-Strong Base Titrations

$CH_3COOH\ (aq) + NaOH\ (aq) \longrightarrow CH_3COONa\ (aq) + H_2O\ (l)$

$CH_3COOH\ (aq) + OH^-\ (aq) \longrightarrow CH_3COO^-\ (aq) + H_2O\ (l)$

At equivalence point (pH > 7):

$CH_3COO^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + CH_3COOH\ (aq)$



Volume NaOH added (mL)	pH
0.0	2.87
5.0	4.14
10.0	4.57
15.0	4.92
20.0	5.35
22.0	5.61
24.0	6.12
25.0	8.72
26.0	10.29
28.0	11.75
30.0	11.96
35.0	12.22
40.0	12.36
45.0	12.46
50.0	12.52

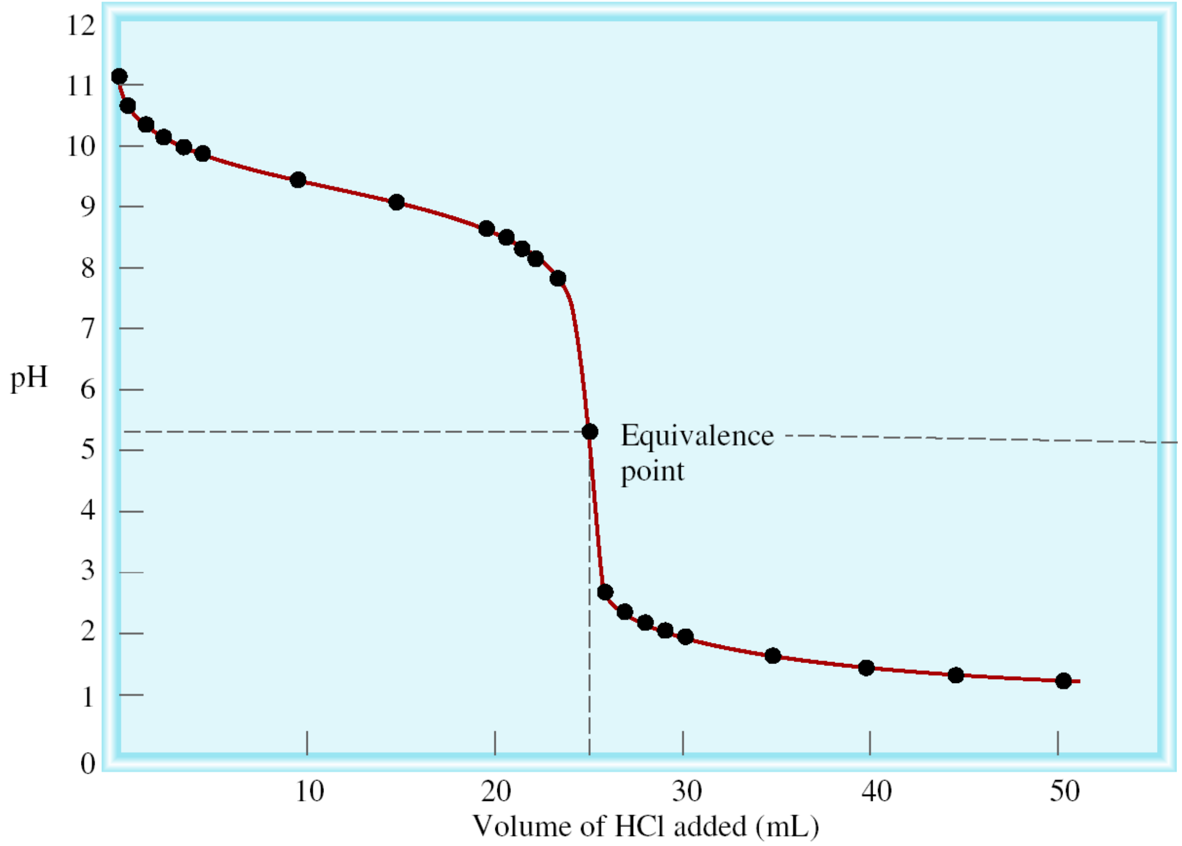
Strong Acid-Weak Base Titrations

$$HCl\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$$

$$H^+\ (aq) + NH_3\ (aq) \longrightarrow NH_4Cl\ (aq)$$

At equivalence point (pH < 7):

$$NH_4^+\ (aq) + H_2O\ (l) \rightleftharpoons NH_3\ (aq) + H^+\ (aq)$$



Volume HCl added (mL)	pH
0.0	11.13
5.0	9.86
10.0	9.44
15.0	9.08
20.0	8.66
22.0	8.39
24.0	7.88
25.0	5.28
26.0	2.70
28.0	2.22
30.0	2.00
35.0	1.70
40.0	1.52
45.0	1.40
50.0	1.30

Exactly 100 mL of 0.10 *M* HNO_2 are titrated with a 0.10 *M* NaOH solution. What is the pH at the equivalence point ?

$$HNO_2\ (aq) + OH^-\ (aq) \longrightarrow NO_2^-\ (aq) + H_2O\ (l)$$

	HNO_2	OH^-	NO_2^-
start (moles)	0.01	0.01	
end (moles)	0.0	0.0	0.01

Final volume = 200 mL

$$[NO_2^-] = \frac{0.01}{0.200} = 0.05\ M$$

$$NO_2^-\ (aq) + H_2O\ (l) \rightleftharpoons OH^-\ (aq) + HNO_2\ (aq)$$

	NO_2^-	OH^-	HNO_2
Initial (*M*)	0.05	0.00	0.00
Change (*M*)	$-x$	$+x$	$+x$
Equilibrium (*M*)	$0.05 - x$	x	x

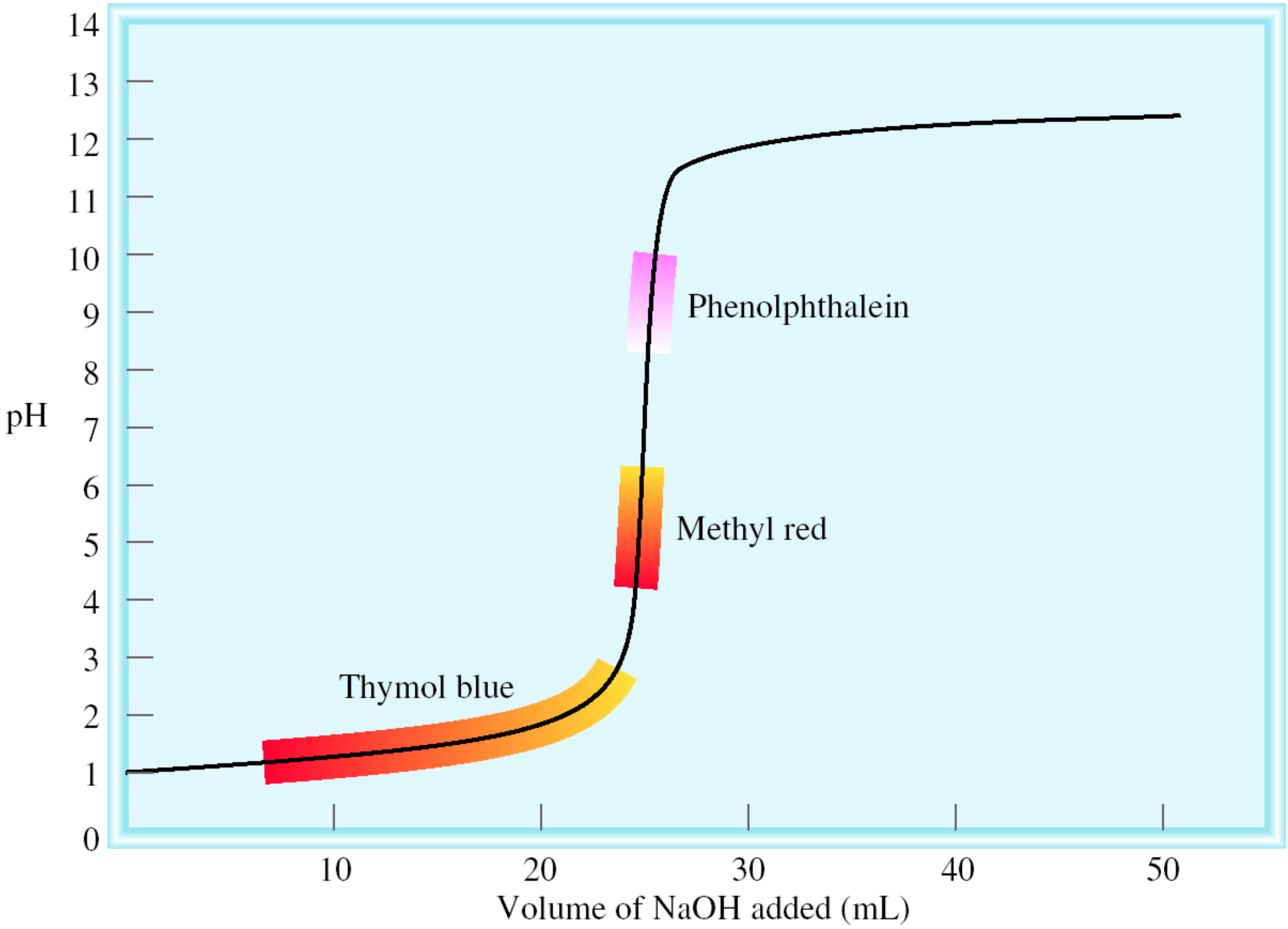
$$K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.05-x} = 2.2 \times 10^{-11}$$

$0.05 – x \approx 0.05$ $\quad x \approx 1.05 \times 10^{-6} = [OH^-]$

pOH = 5.98

pH = 14 – pOH = 8.02

The titration curve of a strong acid with a strong base.



Which indicator(s) would you use for a titration of HNO_2 with KOH ?

Weak acid titrated with strong base.

At equivalence point, will have conjugate base of weak acid.

At equivalence point, pH > 7

Use cresol red or phenolphthalein

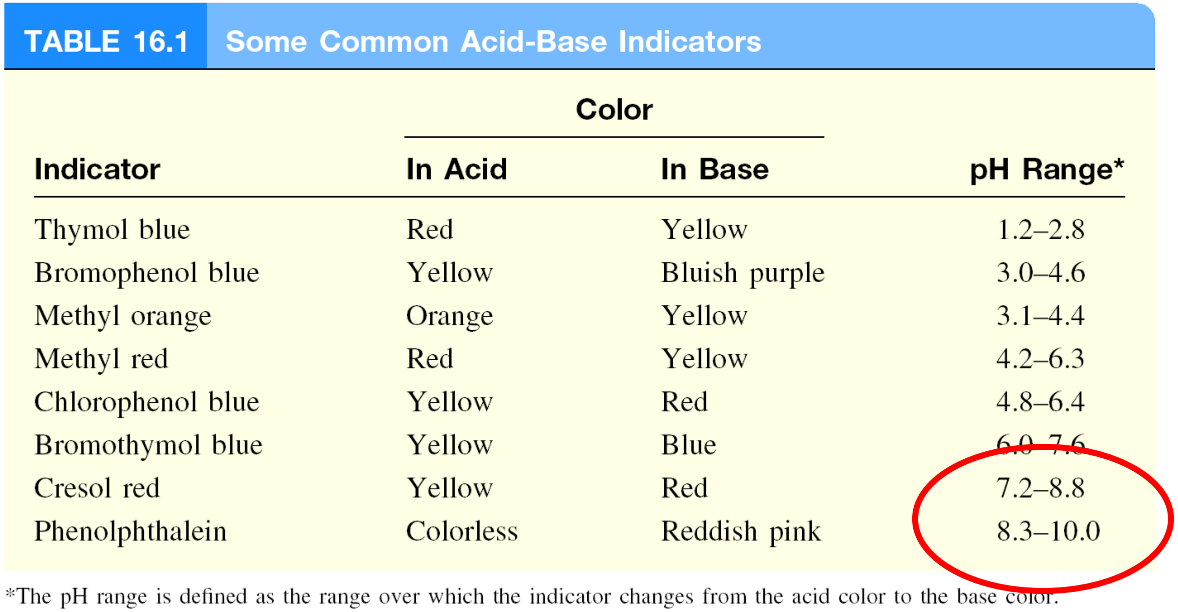
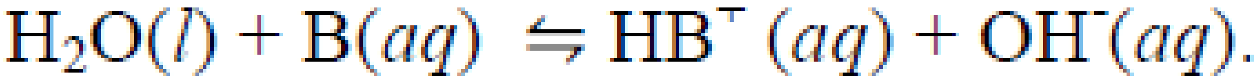


TABLE 16.1 Some Common Acid-Base Indicators

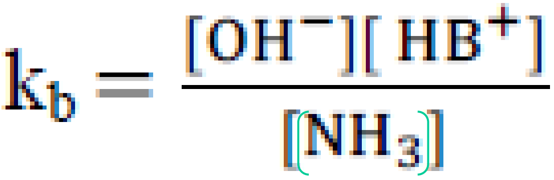
Indicator	Color In Acid	 In Base	pH Range*
Thymol blue	Red	Yellow	1.2–2.8
Bromophenol blue	Yellow	Bluish purple	3.0–4.6
Methyl orange	Orange	Yellow	3.1–4.4
Methyl red	Red	Yellow	4.2–6.3
Chlorophenol blue	Yellow	Red	4.8–6.4
Bromothymol blue	Yellow	Blue	6.0–7.6
Cresol red	Yellow	Red	7.2–8.8
Phenolphthalein	Colorless	Reddish pink	8.3–10.0

*The pH range is defined as the range over which the indicator changes from the acid color to the base color.

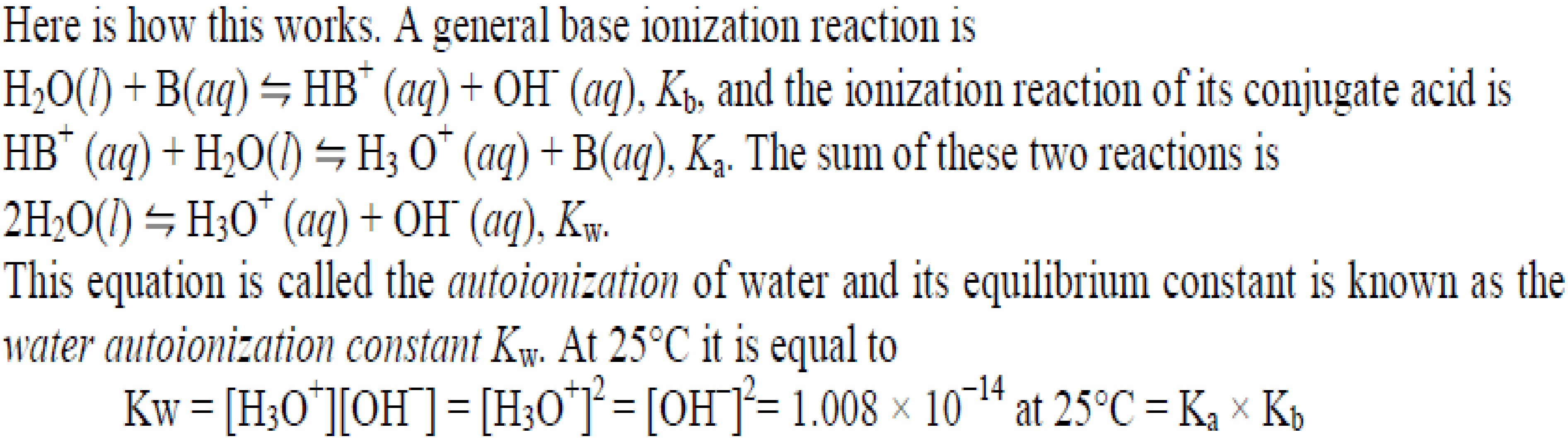
Water auto-ionization constant *K*w



$$H_2O(l) + B(aq) \leftrightharpoons HB^+ (aq) + OH^-(aq).$$



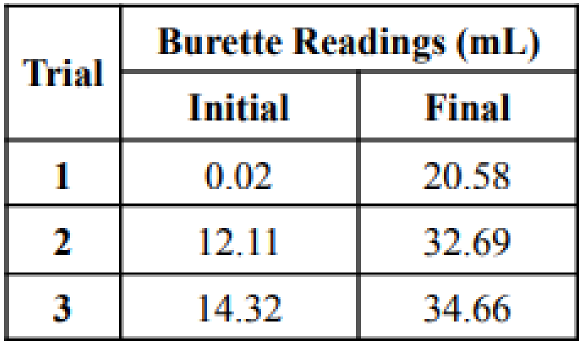
$$k_b = \frac{[OH^-][HB^+]}{[NH_3]}$$



Here is how this works. A general base ionization reaction is
$H_2O(l) + B(aq) \leftrightharpoons HB^+ (aq) + OH^- (aq)$, K_b, and the ionization reaction of its conjugate acid is
$HB^+ (aq) + H_2O(l) \leftrightharpoons H_3O^+ (aq) + B(aq)$, K_a. The sum of these two reactions is
$2H_2O(l) \leftrightharpoons H_3O^+ (aq) + OH^- (aq)$, K_w.
This equation is called the *autoionization* of water and its equilibrium constant is known as the *water autoionization constant* K_w. At 25°C it is equal to

$$Kw = [H_3O^+][OH^-] = [H_3O^+]^2 = [OH^-]^2 = 1.008 \times 10^{-14} \text{ at } 25°C = K_a \times K_b$$

1. In the titration of 25.00 mL of 0.100 M HCl with 0.100 M NaOH, what is the pH of the solution after 15.00 mL of the standard NaOH solution has been added?
2. When titrating 20.00 mL of 0.12 M HCN with 0.08 M NaOH, you have reached the equivalence point when you add 30.00 mL of the NaOH. What is the pH at this point? K_a for HCN is 6.2×10^{-10}
3. 1.0 g of an unknown acid was dissolved in 100 mL of water. 25.00 mL of this solution was titrated with 0.100 M KOH, and the experimental data is shown below. What is the identity of the acid?



Trial	**Burette Readings (mL)**	
	Initial	**Final**
1	0.02	20.58
2	12.11	32.69
3	14.32	34.66

Solubility Equilibria

$$\mathrm{AgCl}\ (s) \rightleftharpoons \mathrm{Ag^+}\ (aq) + \mathrm{Cl^-}\ (aq)$$

$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$ **K_{sp} is the *solubility product constant***

$\mathrm{MgF_2}\ (s) \rightleftharpoons \mathrm{Mg^{2+}}\ (aq) + \mathrm{2F^-}\ (aq)$ $K_{sp} = [\mathrm{Mg^{2+}}][\mathrm{F^-}]^2$

$\mathrm{Ag_2CO_3}\ (s) \rightleftharpoons \mathrm{2Ag^+}\ (aq) + \mathrm{CO_3^{2-}}\ (aq)$ $K_{sp} = [\mathrm{Ag^+}]^2[\mathrm{CO_3^{2-}}]$

$\mathrm{Ca_3(PO_4)_2}\ (s) \rightleftharpoons \mathrm{3Ca^{2+}}\ (aq) + \mathrm{2PO_4^{3-}}\ (aq)$ $K_{sp} = [\mathrm{Ca^{2+}}]^3[\mathrm{PO_4^{3-}}]^2$

Dissolution of an ionic solid in aqueous solution:

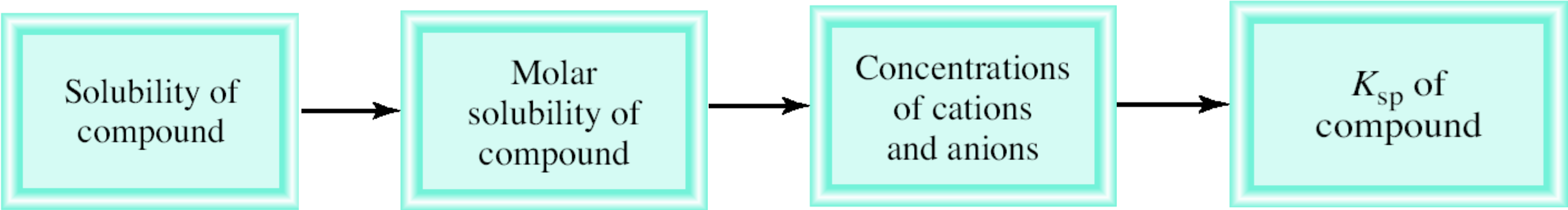
$Q < K_{sp}$	Unsaturated solution	No precipitate
$Q = K_{sp}$	Saturated solution	
$Q > K_{sp}$	Supersaturated solution	Precipitate will form

Solubility Products of Some Slightly Soluble Ionic Compounds at 25°C

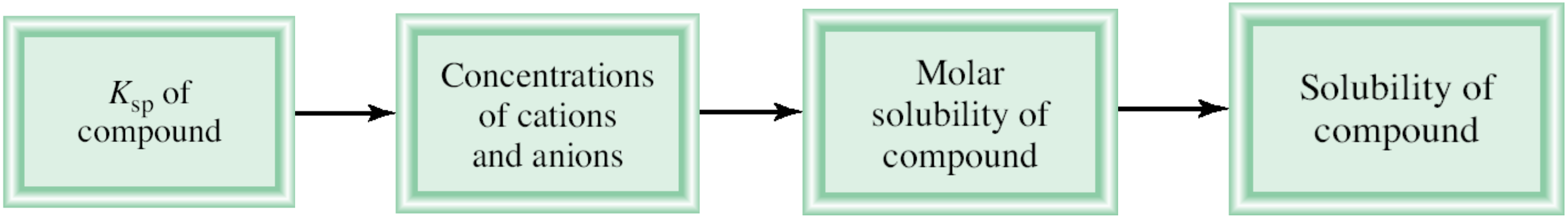
Compound	K_{sp}	Compound	K_{sp}
Aluminum hydroxide [$Al(OH)_3$]	1.8×10^{-33}	Lead(II) chromate ($PbCrO_4$)	2.0×10^{-14}
Barium carbonate ($BaCO_3$)	8.1×10^{-9}	Lead(II) fluoride (PbF_2)	4.1×10^{-8}
Barium fluoride (BaF_2)	1.7×10^{-6}	Lead(II) iodide (PbI_2)	1.4×10^{-8}
Barium sulfate ($BaSO_4$)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi_2S_3)	1.6×10^{-72}	Magnesium carbonate ($MgCO_3$)	4.0×10^{-5}
Cadmium sulfide (CdS)	8.0×10^{-28}	Magnesium hydroxide [$Mg(OH)_2$]	1.2×10^{-11}
Calcium carbonate ($CaCO_3$)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF_2)	4.0×10^{-11}	Mercury(I) chloride (Hg_2Cl_2)	3.5×10^{-18}
Calcium hydroxide [$Ca(OH)_2$]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [$Ca_3(PO_4)_2$]	1.2×10^{-26}	Nickel(II) sulfide (NiS)	1.4×10^{-24}
Chromium(III) hydroxide [$Cr(OH)_3$]	3.0×10^{-29}	Silver bromide ($AgBr$)	7.7×10^{-13}
Cobalt(II) sulfide (CoS)	4.0×10^{-21}	Silver carbonate (Ag_2CO_3)	8.1×10^{-12}
Copper(I) bromide ($CuBr$)	4.2×10^{-8}	Silver chloride ($AgCl$)	1.6×10^{-10}
Copper(I) iodide (CuI)	5.1×10^{-12}	Silver iodide (AgI)	8.3×10^{-17}
Copper(II) hydroxide [$Cu(OH)_2$]	2.2×10^{-20}	Silver sulfate (Ag_2SO_4)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag_2S)	6.0×10^{-51}
Iron(II) hydroxide [$Fe(OH)_2$]	1.6×10^{-14}	Strontium carbonate ($SrCO_3$)	1.6×10^{-9}
Iron(III) hydroxide [$Fe(OH)_3$]	1.1×10^{-36}	Strontium sulfate ($SrSO_4$)	3.8×10^{-7}
Iron(II) sulfide (FeS)	6.0×10^{-19}	Tin(II) sulfide (SnS)	1.0×10^{-26}
Lead(II) carbonate ($PbCO_3$)	3.3×10^{-14}	Zinc hydroxide [$Zn(OH)_2$]	1.8×10^{-14}
Lead(II) chloride ($PbCl_2$)	2.4×10^{-4}	Zinc sulfide (ZnS)	3.0×10^{-23}

Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

Solubility (g/L) is the number of grams of solute dissolved in 1 L of a saturated solution.



Solubility of compound → Molar solubility of compound → Concentrations of cations and anions → K_{sp} of compound



K_{sp} of compound → Concentrations of cations and anions → Molar solubility of compound → Solubility of compound

What is the solubility of silver chloride in g/L ?

$$\mathrm{AgCl}\,(s) \rightleftharpoons \mathrm{Ag^+}\,(aq) + \mathrm{Cl^-}\,(aq)$$

Initial (M)	0.00	0.00
Change (M)	$+s$	$+s$
Equilibrium (M)	s	s

$K_{sp} = 1.6 \times 10^{-10}$

$K_{sp} = [\mathrm{Ag^+}][\mathrm{Cl^-}]$

$K_{sp} = s^2$

$s = \sqrt{K_{sp}}$

$s = 1.3 \times 10^{-5}$

$[\mathrm{Ag^+}] = 1.3 \times 10^{-5}\ M$ $[\mathrm{Cl^-}] = 1.3 \times 10^{-5}\ M$

$$\text{Solubility of AgCl} = \frac{1.3 \times 10^{-5}\ \cancel{\text{mol AgCl}}}{1\ \text{L soln}} \times \frac{143.35\ \text{g AgCl}}{1\ \cancel{\text{mol AgCl}}} = 1.9 \times 10^{-3}\ \text{g/L}$$

Relationship Between K_{sp} and Molar Solubility (s)

Compound	K_{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
$AgCl$	$[Ag^+][Cl^-]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
$BaSO_4$	$[Ba^{2+}][SO_4^{2-}]$	s	s	$K_{sp} = s^2;\ s = (K_{sp})^{\frac{1}{2}}$
Ag_2CO_3	$[Ag^+]^2[CO_3^{2-}]$	$2s$	s	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	s	$2s$	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	s	$3s$	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	$3s$	$2s$	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

If 2.00 mL of 0.200 *M* NaOH are added to 1.00 L of 0.100 *M* $CaCl_2$, will a precipitate form?

The ions present in solution are Na^+, OH^-, Ca^{2+}, Cl^-.

Only possible precipitate is $Ca(OH)_2$ (solubility rules).

Is $Q > K_{sp}$ for $Ca(OH)_2$?

$[Ca^{2+}]_0 = 0.100\ M$ $[OH^-]_0 = 4.0 \times 10^{-4}\ M$

$Q = [Ca^{2+}]_0[OH^-]_0^2 = 0.10 \times (4.0 \times 10^{-4})^2 = 1.6 \times 10^{-8}$

$K_{sp} = [Ca^{2+}][OH^-]^2 = 8.0 \times 10^{-6}$ is given as a constant

$Q < K_{sp}$ No precipitate will form

What concentration of Ag is required to precipitate only AgBr in a solution that contains both Br^- and Cl^- at a concentration of 0.02 *M*?

$$AgBr\,(s) \rightleftharpoons Ag^+\,(aq) + Br^-\,(aq) \qquad K_{sp} = 7.7 \times 10^{-13}$$

$$K_{sp} = [Ag^+][Br^-]$$

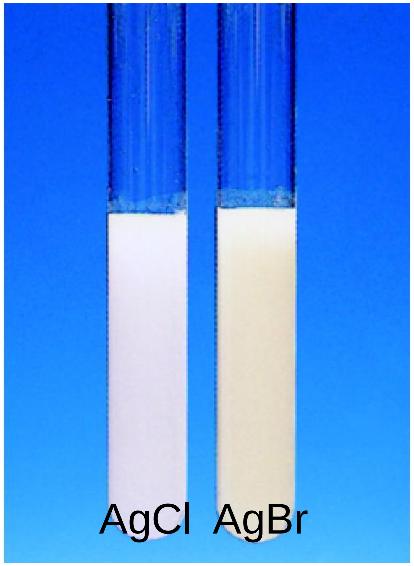
$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11}\ M$$

$$AgCl\,(s) \rightleftharpoons Ag^+\,(aq) + Cl^-\,(aq) \qquad K_{sp} = 1.6 \times 10^{-10}$$

$$K_{sp} = [Ag^+][Cl^-]$$

$$[Ag^+] = \frac{K_{sp}}{[Cl^-]} = \frac{1.6 \times 10^{-10}}{0.020} = 8.0 \times 10^{-9}\ M$$

$$3.9 \times 10^{-11}\ M < [Ag^+] < 8.0 \times 10^{-9}\ M$$



The Common Ion Effect and Solubility

The presence of a common ion **decreases** the solubility of the salt.

What is the molar solubility of AgBr in (a) pure water and (b) 0.0010 *M* NaBr?

$$\mathrm{AgBr}\ (s) \rightleftharpoons \mathrm{Ag^+}\ (aq) + \mathrm{Br^-}\ (aq)$$

$K_{sp} = 7.7 \times 10^{-13}$

$s^2 = K_{sp}$

$\boxed{s = 8.8 \times 10^{-7}}$

$$\mathrm{NaBr}\ (s) \longrightarrow \mathrm{Na^+}\ (aq) + \mathrm{Br^-}\ (aq)$$

$[\mathrm{Br^-}] = 0.0010\ M$

$$\mathrm{AgBr}\ (s) \rightleftharpoons \mathrm{Ag^+}\ (aq) + \boxed{\mathrm{Br^-}}\ (aq)$$

$$\longleftarrow$$

$[\mathrm{Ag^+}] = s$

$[\mathrm{Br^-}] = 0.0010 + s \approx 0.0010$

$K_{sp} = 0.0010 \times s$

$\boxed{s = 7.7 \times 10^{-10}}$

pH and Solubility

- The presence of a common ion **decreases** the solubility.

- Insoluble bases dissolve in acidic solutions

- Insoluble acids dissolve in basic solutions

remove

$$Mg(OH)_2\ (s) \rightleftharpoons Mg^{2+}\ (aq) + 2OH^-\ (aq)$$

add

$\longleftrightarrow$

$$K_{sp} = [Mg^{2+}][OH^-]^2 = 1.2 \times 10^{-11}$$

$$K_{sp} = (s)(2s)^2 = 4s^3$$

$$4s^3 = 1.2 \times 10^{-11}$$

$$s = 1.4 \times 10^{-4}\ M$$

$$[OH^-] = 2s = 2.8 \times 10^{-4}\ M$$

$$pOH = 3.55 \quad pH = 10.45$$

At pH less than 10.45

Lower $[OH^-]$

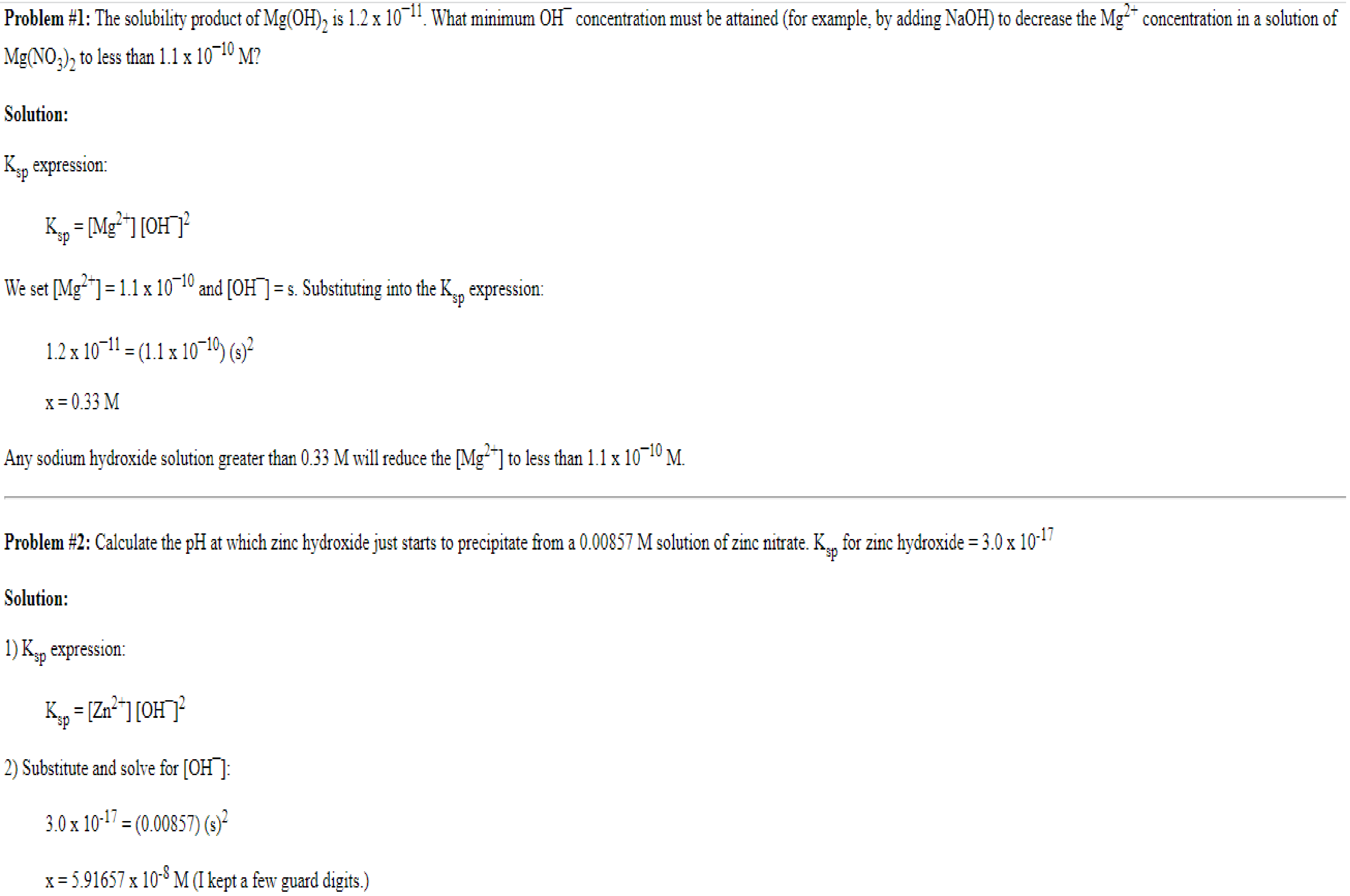
$$OH^-\ (aq) + H^+\ (aq) \longrightarrow H_2O\ (l)$$

Increase solubility of $Mg(OH)_2$

At pH greater than 10.45

Raise $[OH^-]$

Decrease solubility of $Mg(OH)_2$



Problem #1: The solubility product of $Mg(OH)_2$ is 1.2×10^{-11}. What minimum OH^- concentration must be attained (for example, by adding NaOH) to decrease the Mg^{2+} concentration in a solution of $Mg(NO_3)_2$ to less than 1.1×10^{-10} M?

Solution:

K_{sp} expression:

$$K_{sp} = [Mg^{2+}] [OH^-]^2$$

We set $[Mg^{2+}] = 1.1 \times 10^{-10}$ and $[OH^-] = s$. Substituting into the K_{sp} expression:

$$1.2 \times 10^{-11} = (1.1 \times 10^{-10}) (s)^2$$

$$x = 0.33 \text{ M}$$

Any sodium hydroxide solution greater than 0.33 M will reduce the $[Mg^{2+}]$ to less than 1.1×10^{-10} M.

Problem #2: Calculate the pH at which zinc hydroxide just starts to precipitate from a 0.00857 M solution of zinc nitrate. K_{sp} for zinc hydroxide = 3.0×10^{-17}

Solution:

1) K_{sp} expression:

$$K_{sp} = [Zn^{2+}] [OH^-]^2$$

2) Substitute and solve for $[OH^-]$:

$$3.0 \times 10^{-17} = (0.00857) (s)^2$$

$x = 5.91657 \times 10^{-8}$ M (I kept a few guard digits.)

pOH = 7.228 and pH = 6.772

Problem #3: Calculate the number of moles of Ag_2CrO_4 that will dissolve in 1.00 L of 0.010 M K_2CrO_4 solution. K_{sp} for $Ag_2CrO_4 = 9.0 \times 10^{-12}$.

Solution:

1) Concentration of dichromate ion from potassium chromate:

0.010 M

2) Calculate solubility of Ag^+:

$K_{sp} = [Ag^+]^2 [CrO_4^{2-}]$

$9.0 \times 10^{-12} = (s)^2 (0.010)$

$x = 3.0 \times 10^{-5}$ M

Since there is a 2:1 ratio between the moles of aqueous silver ion and the moles of silver chromate that dissolved, 1.5×10^{-5} M is the molar solubility of Ag_2CrO_4 in 0.010 M K_2CrO_4 solution.

Since we were asked for the moles of silver chromate that would disolve in 1.00 L, the final answer is:

1.5×10^{-5} mol

Problem #4: What is the maximum concentration of Mg^{2+} ion that can remain dissolved in a solution that contains 0.7147 M NH_3 and 0.2073 M NH_4Cl? (K_{sp} for $Mg(OH)_2$ is 1.2×10^{-11}; K_b for NH_3 is 1.77×10^{-5})

Solution:

1) Use the acid base data supplied to calculate $[OH^-]$:

$K_b = ([NH_4^+] [OH^-]) / [NH_3]$

$1.77 \times 10^{-5} = [(0.2073) (x)] / 0.7147$

$x = 6.10 \times 10^{-5}$ M

2) Use the K_{sp} expression to calculate the $[Mg^{2+}]$:

$K_{sp} = [Mg^{2+}] [OH^-]^2$

$1.2 \times 10^{-11} = (s) (6.10 \times 10^{-5})^2$

$s = 3.2 \times 10^{-3}$ M

Problem #6: The K_{sp} of AgBr is 5.4×10^{-13} at 25 °C. Calculate the molar solubility of AgBr in 0.050 M $AgNO_3(aq)$ at 25 °C.

Solution:

$K_{sp} = [Ag^+] [Br^-]$

The solution already contains 0.050 M Ag^+ from the dissociation of the $AgNO_3$.

The solution will also contain additional Ag^+, due to the dissociation of the AgBr. This value is small compared to 0.050 M, it can be ignored.

Substitute into K_{sp} equation:

$5.4 \times 10^{-13} = (0.050)\ (s)$

$s = (5.4 \times 10^{-13}) / 0.050$

$s = 1.08 \times 10^{-11}$ M

To two significant digits, the bromide concentration is 1.1×10^{-11} mol/L

If you decided that the additional amount of silver ion CANNOT be ignored, you would have this:

$5.4 \times 10^{-13} = (0.050 + s)\ (s)$

The produces a quadratic:

$s^2 + 0.05s - 5.4 \times 10^{-13} = 0$

Substituting into a quadratic solver gives:

$1.0799999997667 \times 10^{-11}$