Aqueous Equilibria: Applications

Buffers, resist pH changes

pH during titrations

Solubility equilibria of salts, K_{sp}

Common Ion Effects

Complex equilibria

K_a or K_b + K_{sp}

Buffers

Buffer solutions contain a significant concentration of both the weak acid and its conjugate weak base

Buffer solutions resist changes in pH when either an acid or base is added

Buffers

$HA_{(aq)} + HOH_{(aq)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq}$

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

Both must be present
In the solution

A buffer solution is prepared by adding the weak acid <u>and</u> the salt of its conjugate acid.

Buffers

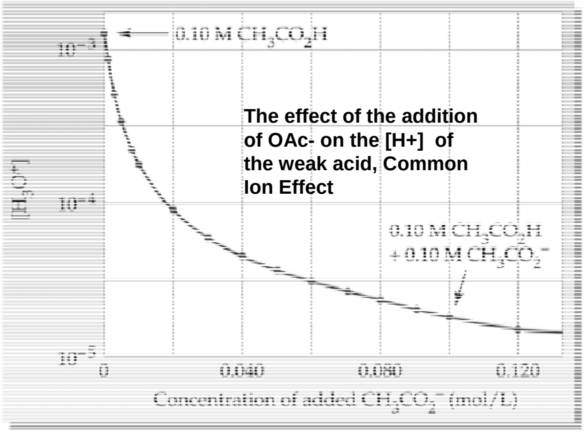
When a <u>weak acid</u> and the salt of its <u>conjugate base</u> are combined in a solution (forming a Buffer) the influence that the conjugate base has on the properties of the solution is called a <u>Common Ion Effect</u>.

This term arises from the fact that the conjugate base is present in two separate equilibrium equations

$$HA_{(aq)} + HOH_{(aq)} \rightarrow H_3O^+_{(aq)} + A^-_{(aq)} \qquad K_a$$

$$A^-_{(aq)} + HOH_{(l)} \rightarrow HA_{(aq)} + OH_{(aq)} \qquad K_b$$

Common Ion Effects are more aptly considered in relation to Solubility



The effect of the addition of OAc- on the [H+] of the weak acid, Common Ion Effect

Buffers

If 0.1 mole of HOAc and 0.075 mole of NaOAc are combined in a solution with a total volume of 1 liter, what will the pH be at equilibrium?

	$HOAc_{(aq)}$ + $HOH_{(aq)}$ →	$H_3O^+_{(aq)}$ +	$Ac^-_{(aq}$
Initial	**0.1 M**	**10^{-7}M**	**0.075M**
Equilibrium	**0.1-x M**	**10^{-7} + x M**	**0.075 –x M**

$$K_a = \frac{[A-][H+]}{[HA]} = \frac{(0.075 + x)(10^{-7} + x)}{(0.1-x)} = 1.8 \times 10^{-5}$$

Buffers cont'd

$$K_a = \frac{[A-][H+]}{[HA]} = \frac{(0.075 + x)(10^{-7} + x)}{(0.1 - x)} = 1.8 \times 10^{-5}$$

When x << [HA] and [A-] then solution is easy!

$$1.8 \times 10^{-5} = \frac{(0.075)(x)}{0.1}$$

$$X = [H+] = \frac{1.8 \times 10^{-5}(0.1)}{0.075} = 2.4 \times 10^{-5} M$$

$$pH = 4.6$$

Buffers cont'd

$$K_a = \frac{[A-][H+]}{[HA]} = \frac{(0.075 + x)(10^{-7} + x)}{(0.1 - x)} = 1.8 \times 10^{-5}$$

$$\text{Log } K_a = \text{Log}\left(\frac{[A-][H+]}{[HA]}\right) = \text{Log } \frac{[A-]}{[HA]} + \text{Log}[H+]$$

X -1

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

Buffers cont'd

$$K_a = \frac{[A-][H+]}{[HA]} = \frac{(0.075 + x)(10^{-7} + x)}{(0.1 - x)} = 1.8 \times 10^{-5}$$

$$-\log Ka = pKa = -\log \frac{[A-]}{[HA]} + pH$$

$$pH = pKa + \log \frac{[A-]}{[HA]}$$ Henderson-Hasselbalch eqn

Buffers cont'd

$\text{pH} = \text{pKa} + \log \frac{[A\ ]}{[HA]}$ Henderson-Hasselbalch eqn

A buffer is effective when the ratio $\frac{[A\ ]}{[HA]}$ remains within the limits of 1/10 and 10/1

The pH is buffered then for a pH range of pKa ± 1.0

Because

The log 0.1 is- 1 and The log of 10 is +1

Buffer Problem

5 g of lactic acid ($C_3H_3O_3H$) and 5 g of potassium lactate are dissolved in 100 mL of water to form a buffer solution. The Ka of lactic acid is 1.4×10^{-4}M. What is the equilibrium pH?

Mwt HLac = 90 g/mole Mwt KLac = 128 g/mole

[HLac] = 0.555 M [KLac] = 0.39 M

	$HLac_{(aq)}$ +	$HOH_{(aq)} \rightarrow$	$H_3O^+_{(aq)}$ +	$Lac^-_{(aq}$
Initial	0.555 M		10^{-7}M	0.39M
Equilibrium	0.555-x M		10^{-7} + x M	0.39 +x M

$$K_a = \frac{[A-][H+]}{[HA]} = \frac{(0.39 + x)(10^{-7} + x)}{(0.555-x)} = 1.4 \times 10^{-4}$$

Buffer Problem

$$K_a = \frac{[A^-][H^+]}{[HA]} = \frac{(0.39 + x)(10^{-7} + x)}{(0.555-x)} = 1.4 \times 10^{-4}$$

If x << [HA] and [A-] then

K_a (0.555/0.39) = $[H^+] = 1.9 \times 10^{-4}$ M ☑

pH = 3.7 ☑

or using the Henderson-Hasselbalch eqn

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

pH = 3.85 + log (0.39/0.555) = 3.85 + log 0.7

= 3.85 - 0.15

= 3.7 ☑

The pH changes that accompany neutralization reactions

Consider the titration of 25.00 mL of a 0.1M HCl solution with a 0.1M NaOH solution.

How does the pH in a solution of a strong acid change during a neutralization?

Strong acids and Strong Bases

react completely so the base will be consumed and pH will be determined by the excess HCl until an equivalent amount of base has been added after this point the base will be in excess and will determine the pH

The pH changes that accompany neutralization reactions

Consider the titration of 25.00 mL of a 0.1M HCl solution with a 0.1M NaOH solution.

Points during the titration to consider

1) initial pH before addition of base
2) pH during titration prior to the equivalence point
3) pH at the equivalence point
4) pH after the equivalence point

The pH changes that accompany neutralization reactions

Consider the titration of 25.00 mL of a 0.1M HCl solution with a 0.1M NaOH solution.

1) initial pH before addition of base

pH is determined by ionization of the strong acid and [HCl] = [H^+] = 0.1M

-log (0.1) = **1.0 = pH**

The pH changes that accompany neutralization reactions

Consider the titration of 25.00 mL of a 0.1M HCl solution with a 0.1M NaOH solution.

2) pH during titration prior to the equivalence point

Consider pH after 5, 12.5 and 24 ml of added base

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

The pH changes that accompany neutralization reactions

Consider pH after 5, 12.5, and 24 ml of added base

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

Initial amount of HCl present

0.025L HCl x 0.1 M = 2.5×10^{-3} mole HCl

Added moles of NaOH

a) 5 mL 0.1 M NaOH → 5.0×10^{-4} mole NaOH

b) 12.5 mL 0.1 M NaOH → 1.25×10^{-3} mole NaOH

c) 24 mL 0.1 M NaOH → 2.4×10^{-3} mole NaOH

The pH changes prior to the Equivalence point

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

	moles	**moles**	**Volume total (L)**
Initial	**2.5×10^{-3}**	**0**	**0.025**
a)		**5.0×10^{-4}**	**0.030**
b)		**1.25×10^{-3}**	**0.0375**
c)		**2.4×10^{-3}**	**0.049**

$[H^+]$ after rxn = (Initial Moles HCl – Moles NaOH added)/V_t

a) 2.0×10^{-3} mole HCl → [H+] = 6.67×10^{-2} M pH = 1.18

b) 1.25×10^{-3} mole HCl → [H+] = 3.33×10^{-2} M pH = 1.47

c) 1.0×10^{-4} mole HCl → [H+] = 2.04×10^{-3} M pH = 2.69

The pH changes cont'd
The equivalence point

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

Moles	Moles	Moles	Volume total (L)
Initial	2.5×10^{-3}	0	0.025
Equivalence pt		2.5×10^{-3}	0.050

All HCl is converted to H_2O with no Excess of NaOH so the pH is determined by the autoionization of H_2O

Moles at Equiv pt.	0	0

d) $K_w = 1.0\ 10^{-14} = [H^+][OH^-]$

$[H^+] = [OH^-]$ 1.00×10^{-7} M pH = 7.00

The pH changes after the equivalence point

Consider pH after 26, 37.5, and 50 ml of added base

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

Initial amount of HCl present

0.025L HCl x 0.1 M = 2.5×10^{-3} mole HCl

Added moles of NaOH (exceeds initial HCl !!)

e) 26 mL 0.1 M NaOH → 2.60×10^{-3} mole NaOH
f) 37.5 mL 0.1 M NaOH → 3.75×10^{-3} mole NaOH
g) 50 mL 0.1 M NaOH → 5.0×10^{-3} mole NaOH

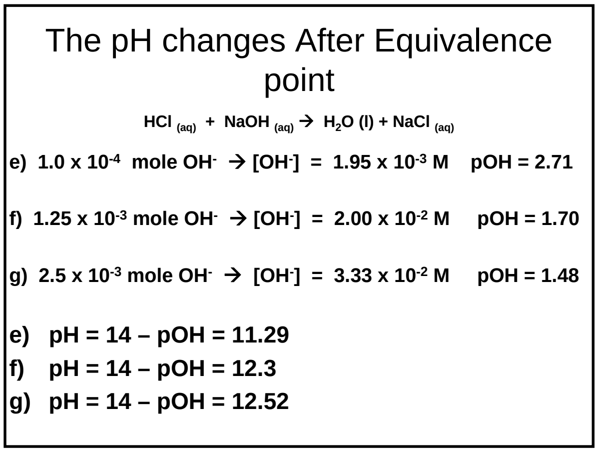
The pH changes after
The Equivalence point

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

Moles	Moles	Moles	Volume total (L)
Initial	2.5×10^{-3}	0	0.025
e)		2.60×10^{-3}	0.051
f)		3.75×10^{-3}	0.0625
g)		5.0×10^{-3}	0.075

$[OH^-]$ after rxn = (Moles NaOH added-Mole Initial HCl)/Vt

e) 1.0×10^{-4} mole OH- → $[OH^-] = 1.95 \times 10^{-3}$ M pOH =
f) 1.25×10^{-3} mole OH- → $[OH^-] = 2.00 \times 10^{-2}$ M pOH =
g) 2.5×10^{-3} mole OH- → $[OH^-] = 3.33 \times 10^{-3}$ M pOH =



The pH changes After Equivalence point

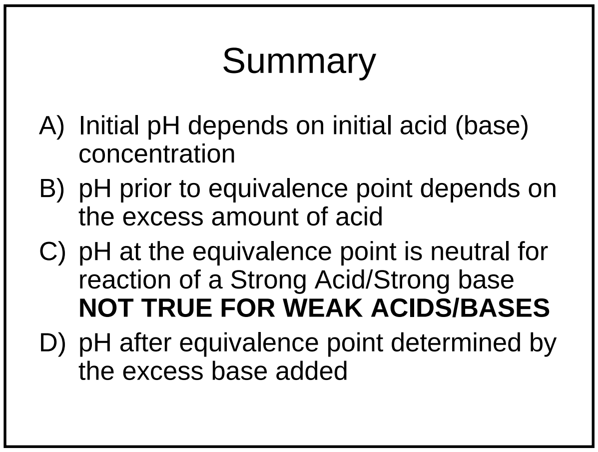
$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

e) 1.0×10^{-4} mole OH^- → $[OH^-]$ = 1.95×10^{-3} M pOH = 2.71

f) 1.25×10^{-3} mole OH^- → $[OH^-]$ = 2.00×10^{-2} M pOH = 1.70

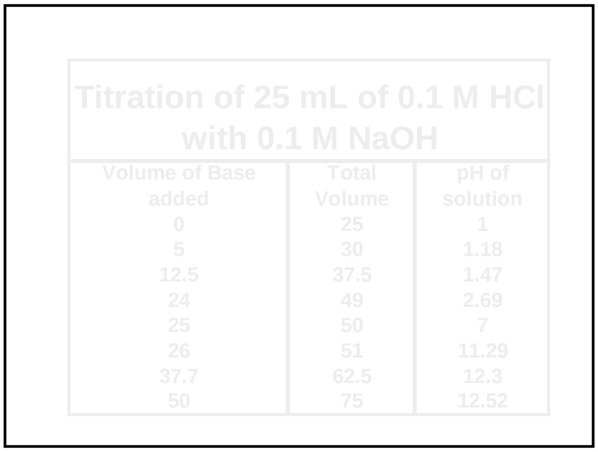
g) 2.5×10^{-3} mole OH^- → $[OH^-]$ = 3.33×10^{-2} M pOH = 1.48

e) pH = 14 – pOH = 11.29
f) pH = 14 – pOH = 12.3
g) pH = 14 – pOH = 12.52



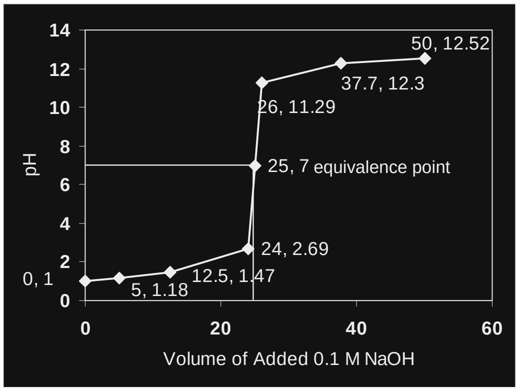
Summary

A) Initial pH depends on initial acid (base) concentration
B) pH prior to equivalence point depends on the excess amount of acid
C) pH at the equivalence point is neutral for reaction of a Strong Acid/Strong base **NOT TRUE FOR WEAK ACIDS/BASES**
D) pH after equivalence point determined by the excess base added



Titration of 25 mL of 0.1 M HCl with 0.1 M NaOH

Volume of Base added	Total Volume	pH of solution
0	25	1
5	30	1.18
12.5	37.5	1.47
24	49	2.69
25	50	7
26	51	11.29
37.7	62.5	12.3
50	75	12.52



pH during the Titration of a Weak Acid with a Strong Base

Consider titration of 25 mL of 0.1 M HOAc, $K_a = 1.8 \times 10^{-5}$, with 0.1 M NaOH.

The same regions as considered for the Strong Acid/Strong base titration must be considered

a) Initial pH
b) pH prior to equivalence point
c) pH at the equivalence point
d) pH following the equivalence point

Initial pH the equilibrium of a Weak Acid

$$\mathbf{HOAc_{(aq)} + HOH_{(aq)} \rightarrow H_3O^+_{(aq)} + OAc^-_{(aq)}}$$

Equilibrium 0.1 –x X X

$$\mathbf{K_a = 1.8 \times 10^{-5} = \frac{x^2}{[0.1-x]}}$$

$x = 1.34 \times 10^{-3}$ M = $[H^+]$ pH = 2.87

The pH changes prior to the Equivalence point

$HOAc_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaOAc_{(aq)}$

Moles	Moles	Moles		Volume total
Initial	2.5×10^{-3}	0		0.025L
a)		5.0×10^{-4}	5.0×10^{-4}	0.03 L
b)		1.25×10^{-3}	1.25×10^{-3}	0.0375
c)		2.4×10^{-3}	2.4×10^{-3}	0.049

[HOAc] after rxn = (Initial HOAc – NaOH)/Vt

a)	2.0×10^{-3} mole HOAc	→ 6.67×10^{-2} M HOAc	
	5.0×10^{-4} mole NaOAc	→ 1.67×10^{-2} M NaOAc	pH = 4.15
b)	1.25×10^{-3} mole HOAc	→ 3.33×10^{-2} M HOAc	
	1.25×10^{-3} mole NaOAc	→ 3.33×10^{-2} M NaOAc	pH = 4.7
c)	1.0×10^{-4} mole HOAc	→ 2.04×10^{-3} M HOAc	
	2.4×10^{-3} mole NaOAc	→ 4.89×10^{-2} M NaOAc	pH = 5.12

solve weak acid equilibrium problem

The pH at the Equivalence point

$HOAc_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaOAc_{(aq)}$

Moles	Moles	Moles	Volume total (L)
Initial	2.5×10^{-3}	0	0.025
		2.5×10^{-3}	0.050

All HOAc has reacted to form H_2O and NaOAc

pH at the equivalence point is determined by the dissociation of the weak base

2.5×10^{-3} mole NaOAc → 5.0×10^{-2} M NaOAc pH = 3.7

solve weak base equilibrium problem, $K_b = K_w/K_a$

$NaOAc_{(aq)} + HOH_{(l)} \leftrightarrows HOAc_{(aq)} + NaOH_{(aq)}$

The pH at the Equivalence point

2.5×10^{-3} mole NaOAc → 5.0×10^{-2} M NaOAc pH = 3.7

solve weak base equilibrium problem, $K_b = K_w/K_a$

	$NaOAc_{(aq)} + HOH_{(l)} \leftrightarrows$	$HOAc_{(aq)}$	$+ NaOH_{(aq)}$
Equilibrium	$2.5 \times 10^{-3} - x$	x	x

$$K_b = \frac{[HOAc][NaOH]}{[NaOAc]} = 5.56 \times 10^{-10}$$

$X = [OH^-] = 1.18 \times 10^{-6}M$ pOH = 5.93

pH = 14 - pOH = 8.07

The pH changes after the equivalence point

Consider pH after 26, 37.5, and 50 ml of added base

No Acid is present – After subtraction of the reacted base this becomes a dilution problem

Initial amount of HCl present

0.025L HCl x 0.1 M = 2.5 x 10^{-3} mole HCl

Added moles of NaOH (exceeds initial HCl !!)

e) 26 mL 0.1 M NaOH → 2.60 x 10^{-3} mole NaOH
f) 37.5 mL 0.1 M NaOH → 3.75 x 10^{-3} mole NaOH
g) 50 mL 0.1 M NaOH → 5.0 x 10^{-3} mole NaOH

The pH changes After Equivalence point

$HOAc_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaOAc_{(aq)}$

Moles	**Moles**	**Moles**	**Volume total (L)**
Initial	**2.5 x 10^{-3}**	**0**	**0.025**
e)		**2.60 x 10^{-3}**	**0.051**
f)		**3.75 x 10^{-3}**	**0.0625**
g)		**5.0 x 10^{-3}**	**0.075**

Excess strong base, $[OH^-]$ after rxn
= (Moles NaOH added - Moles Initial HOAc)/V_t

e) 1.0 x 10^{-4} mole OH- → [OH-] = 1.95 x 10^{-3} M pOH =
f) 1.25 x 10^{-3} mole OH- → [OH-] = 2.00 x 10^{-2} M pOH =
g) 2.5 x 10^{-3} mole OH- → [OH-] = 3.33 x 10^{-3} M pOH =

The pH changes After Equivalence point

$HCl_{(aq)} + NaOH_{(aq)} \rightarrow H_2O\ (l) + NaCl_{(aq)}$

e) 1.0 x 10^{-4} mole OH^- → $[OH^-]$ = 1.95 x 10^{-3} M pOH = 2.71

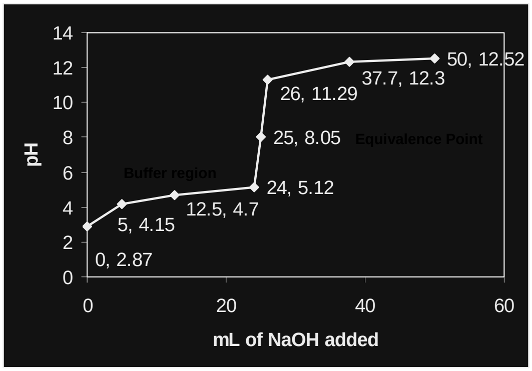
f) 1.25 x 10^{-3} mole OH- → $[OH^-]$ = 2.00 x 10^{-2} M pOH = 1.70

g) 2.5 x 10^{-3} mole OH^- → $[OH^-]$ = 3.33 x 10^{-2} M pOH = 1.48

e) pH = 14 – pOH = 11.29
f) pH = 14 – pOH = 12.3
g) pH = 14 – pOH = 12.52

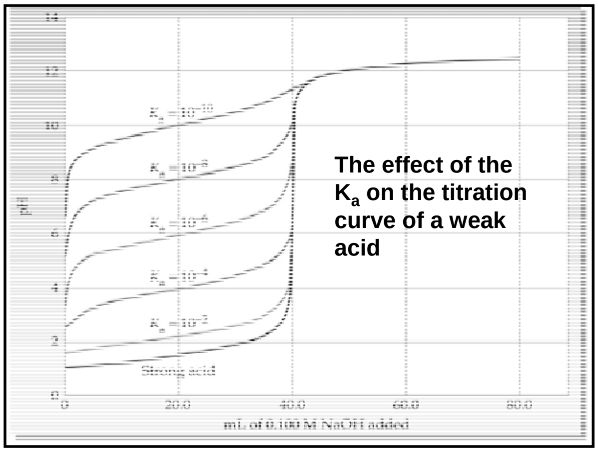
Titration of 25 mL of 0.1 M HOAc with 0.1 M NaOH

Volume of Base added	Total Volume	pH of solution
0	25	2.87
5	30	4.15
12.5	37.5	4.7
24	49	5.12
25	50	8.05
26	51	11.29
37.7	62.5	12.3
50	75	12.52



Important Facts about the Weak Acid Titration Curve

1) The initial pH is calculated by the Weak Acid Equilibrium
2) The region prior to the equivalence point of the titration is called the **Buffer Region**
3) The **pH at ½ the equivalence point** is **equal to the pKa** because [HA] =[NaA]
4) At the equivalence point the pH is calculated by a weak base equilibrium
5) After the equivalence point the pH is controlled by the excess Strong Base



The effect of the K_a on the titration curve of a weak acid

Reaction of a Weak Acid with a Weak base

$HA + B \leftrightarrows BH^+ + A^-$

$H_2O + HA \leftrightarrows A^- + H_3O^+ \qquad K_a$
$H_2O + B \leftrightarrows HB^+ + OH^- \qquad K_b$

$2H_2O + HA + B \leftrightarrows BH^+ + A^- + H_3O^+ + OH^-$
$-[2H_2O \leftrightarrows H_3O^+ + OH^-] \qquad K_w$

$HA + B \leftrightarrows BH^+ + A^- \qquad K = (K_a)(K_b)/K_w$

Reaction of a Weak Acid with a Weak base

$HOAc + CN^- \leftrightarrows HCN + OAc^-$

$H_2O + HOAc \leftrightarrows OAc^- + H_3O^+ \qquad K_a$
$H_2O + CN^- \leftrightarrows HCN + OH^- \qquad K_b$

$HOAc + CN^- \leftrightarrows HCN + OAc^- \quad K = (K_a)(K_b)/K_w$

$K = (1.8 \times 10^{-5})(2.0 \times 10^{-5})/10^{-14}$

$K = 3.6 \times 10^4$

Polyprotic Weak acids

The titration curve of a diprotic weak acid contains two inflection points.

Consider titration of 25 mL of 1.0 M solution H_2A with 1.0 M NaOH

$H_2A + H_2O \leftrightarrows H_3O^+ + HA^-$ $K_{a1} = 4.6 \times 10^{-3}$ $pK_{a1} = 2.34$

$HA^- + H_2O \leftrightarrows H_3O^+ + A^-$ $K_{a2} = 2.0 \times 10^{-10}$ $pK_{a2} = 9.69$

Initial pH is calculated identically to a monoprotic weak acid

$K_{a1} = \frac{[H^+][HA^-]}{[H_2A]} = \frac{x^2}{[1.0 - x]}$ ➔ x = [H+] = 0.066M and pH = 1.18

When 12.5 mL has been added $[H_2A] = [HA^-]$ and $K_{a1} = [H^+]$ $pH = pK_{a1} = 2.34$

When 25 mL has been added (1 eq) Then the solution is equivalent to a solution prepared from NaHA.

Polyprotic Weak acids

Consider titration of 25 mL of 1.0 M solution H_2A with 1.0 M NaOH

1) $H_2A + H_2O \leftrightarrows H_3O^+ + HA^-$ $K_{a1} = 4.6 \times 10^{-3}$ $pK_{a1} = 2.34$

2) $HA^- + H_2O \leftrightarrows H_3O^+ + A^{2-}$ $K_{a2} = 2.0 \times 10^{-10}$ $pK_{a2} = 9.69$

When 25 mL of NaOH has been added (1 eq) Then the solution is equivalent to a solution prepared to be 0.5 M NaHA. NaHA can both lose or gain a proton.
The overall equilibrium is the combination of the two equilibria.

➔ $[HA^-] = 0.5$ M ⬅

$$H_3O^+ + HA^- \leftrightarrows H_2A + H_2O \qquad 1/K_{a1} = 4.6 \times 10^{-3}$$
$$\underline{HA^- + H_2O \leftrightarrows H_3O^+ + A^{2-} \qquad K_{a2} = 2.0 \times 10^{-10}}$$
$$HA^- + HA^- \leftrightarrows H_2A + A^{2-} \qquad K_{eq} = K_{a2}/K_{a1} = 4.3 \times 10^{-8}$$

$$\mathbf{K_{eq} = \frac{[H_2A][A^{2-}]}{[HA\text{-}]^2} = \frac{x^2}{(0.5-x)^2}} \quad ➔ \quad \mathbf{(0.5)(K_{eq})^{1/2} = [H_2A] = [A^{2-}]}$$

But from the eqn 1) $$\mathbf{[H^+] = \frac{K_{a1}[H_2A]}{[HA^-]} = \frac{K_{a1}(0.5)(K_{eq})^{1/2}}{(0.5)} = K_{a1}(K_{a2}/K_{a1})^{1/2} = (K_{a1}K_{a2})^{1/2}}$$

$$\mathbf{pH = -\log (K_{a1}K_{a2})^{1/2} = -1/2 [\log K_{a1} + \log K_{a2}] = \frac{(pK_{a1} + pK_{a2})}{2} = 6.02}$$

Polyprotic Weak acids

Consider titration of 25 mL of 1.0 M solution H_2A with 1.0 M NaOH

1) $H_2A + H_2O \leftrightarrows H_3O^+ + HA\text{-}$ $K_{a1} = 4.6 \times 10^{-3}$ $pK_{a1} = 2.34$

2) $HA^- + H_2O \leftrightarrows H_3O^+ + A^{2-}$ $K_{a2} = 2.0 \times 10^{-10}$ $pK_{a2} = 9.69$

When 37.5 mL has been added (1.5 eq) In this solution $[HA\text{-}] = [A^{2-}]$. The Equilibrium involving these ions is eqn (2) and the pH is

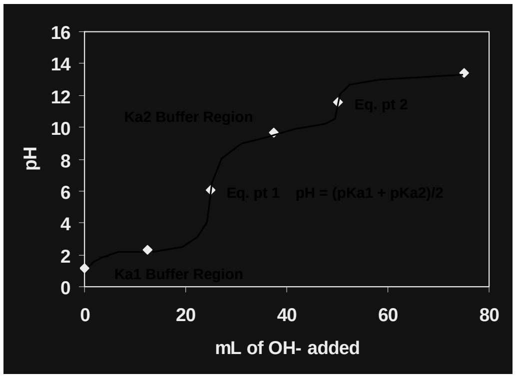
$$\mathbf{K_{a2} = \frac{[H^+][A^{2-}]}{[HA^-]} = [H^+]} \quad ➔➔ \quad \mathbf{pH = pK_{a2} = 9.69}$$

When 50 ml has been added (2 eq) the 2nd equivalance point. The solution is the same as if it were prepared only from the salt of A^{2-} and $[A^{2-}] = 0.33$ M

$$\mathbf{A^{2-} + H_2O \leftrightarrows OH^- + HA^- \qquad K_{b2} = K_w/K_{a2} = 5.0 \times 10^{-5}}$$

$$\mathbf{K_{b2} = \frac{[OH^-][HA^-]}{[A^{2-}]}} \quad ➔ \quad \mathbf{x^2 = 0.33K_{b2}} \quad ➔ \quad \mathbf{x = [OH^-] = 4.06 \times 10^{-3}}$$

$$\mathbf{[H^+] = 2.46 \times 10^{-12} \quad pH = 11.6}$$



Solubility Equilbria

Examples:

$AgCl_{(s)} \rightleftarrows Ag^+_{(aq)} + Cl^-_{(aq)}$

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

$MgF_{2\,(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$

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

$Al(OH)_{3\,(s)} \rightleftarrows Al^{3+}_{(aq)} + 3OH^-_{(aq)}$

$K_{sp} = [Al^{3+}][OH^-]^3$

Note: There is no term in the Equilibrium expression for the solid. It is a pure substance and by definition it has an activity of 1.0

Solubility Product

Problem: If a solution is prepared by dissolving 2 g $Mg(OAc)_2$ and 5 g NaF in 100 mL, will a precipitate form?

Which Solubility should we consider? MgF_2 or NaOAc?

We must remember our solubility facts! All salts of Na+ and OAc- are soluble!

$MgF_{2\,(s)} \rightleftarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$

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

K_{sp} is called the solubility product constant, the value of K_{sp} places an upper limit on the concentrations of the ions involved in the solubility, When the ion product exceeds K_{sp} a solid will exist

Solubility Product

Problem: If a solution is prepared by dissolving 2 g $Mg(OAc)_2$ and 5 g NaF in 100 mL will a precipitate form?

Mwt $Mg(OAc)_2$ = 142.3 g/mole ➔ 2g/142.3 = 0.014 mole ➔ 0.14M $Mg(OAc)_2$

Mwt NaF = 42 g/mole ➔ 5g /42 = 0.119 mole ➔ 1.19 M NaF

$$MgF_{2\,(s)} \leftrightarrows Mg^{2+}{}_{(aq)} + 2F^{-}{}_{(aq)}$$

$$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^{-}]^2$$

$$Q_{ion\ product} = (0.14)(1.19)^2 = 0.19$$

K_{sp} << 0.19 Therefore a PPT forms!

Solubility Equilbria
The Common Ion Effect

Examples:

$$AgCl_{(s)} \leftrightarrows Ag^{+}{}_{(aq)} + Cl^{-}{}_{(aq)}$$

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

$$MgF_{2\,(s)} \leftrightarrows Mg^{2+}{}_{(aq)} + 2F^{-}{}_{(aq)}$$

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

$$Al(OH)_{3\,(s)} \leftrightarrows Al^{3+}{}_{(aq)} + 3OH^{-}{}_{(aq)}$$

$$K_{sp} = [Al^{3+}][OH^{-}]^3$$

If a solution already contains one of the ions present in the solubility equilibrium at an appreciable concentration this will alter the solubility of the salt

Solubility Product

Problem: If excess Hg_2Cl_2 is added to water what is the equilibrium concentration of Cl^-?

Since solid is present **$K_{sp} = 4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2$**

	$Hg_2Cl_{2\,(s)} \leftrightarrows$	$Hg_2^{2+}{}_{(aq)}$	$+ 2Cl^{-}{}_{(aq)}$
pure water		0	0
At equil		x	2x

$$K_{sp}\ 4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2 = (x)(2x)^2$$

$$= 4x^3 \Rightarrow x = (K_{sp}/4)^{1/3}$$

$$x = (1.1 \times 10^{-18})^{1/3} = 1.03 \times 10^{-6}$$

$$[Hg_2^{2+}] = 1.03 \times 10^{-6} \quad [Cl^-] = 2.03 \times 10^{-6}$$

Problem: What is the solubility of Hg_2Cl_2 (MWt = 472g/mole) in g in 1 x 10^3 L of water? To which 58.5 g NaCl is added

Since solid is present $K_{sp} = 4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2$

$Hg_2Cl_{2\,(s)} \leftrightarrows Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$

	Hg_2^{2+}	$2Cl^-$
pure water	0	0
At equil	x	2x

K_{sp} $4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2 = (x)(2x)^2$

$= 4x^3 \Rightarrow x = (K_{sp}/4)^{1/3}$

$x = (1.1 \times 10^{-18})^{1/3} = 1.03 \times 10^{-6}$

$[Hg_2^{2+}] = 1.03 \times 10^{-6}$ $[Cl^-] = 2.03 \times 10^{-6}$

Solubility = x mole/L x V = $1.03 \times 10^{-6} \times 10^3$

$= 1.03 \times 10^{-3}$ mole $Hg_2Cl_2 \Rightarrow 0.486$ g Hg_2Cl_2

Problem: What is the solubility of Hg_2Cl_2 (MWt = 472g/mole) in g in 1 x 10^3 L of water which contains 58.5 g of NaCl?

Since solid is present $K_{sp} = 4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2$

$Hg_2Cl_{2\,(s)} \leftrightarrows Hg_2^{2+}{}_{(aq)} + 2Cl^-{}_{(aq)}$

	Hg_2^{2+}	$2Cl^-$
Salt water	0	10^{-3}
At equilibrium	x	$10^{-3} + 2x$

K_{sp} $4.4 \times 10^{-18} = [Hg_2^{2+}][Cl^-]^2 = (x)(10^{-3} + 2x)^2$

If x<<2x the problem simplifies and

$K_{sp} = (x)(10^{-3})^2 = x10^{-6} \Rightarrow x = (K_{sp}/10^{-6})$

$x = 4.4 \times 10^{-12} = [Hg_2^{2+}] << 10^{-3}$ ☑

Solubility = x mole/L x V = $4.4 \times 10^{-12} \times 10^3$

$= 4.4 \times 10^{-9}$ mole $Hg_2Cl_2 \Rightarrow 2.08 \times 10^{-6}$g Hg_2Cl_2

The Effects of pH on solubility are due to the Common ion Effect, the involvement of one of ions in the solubility in acid/base equilibrium

$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2$

$MgF_{2\,(s)} \leftrightarrows Mg^{2+}{}_{(aq)} + 2F^-{}_{(aq)}$

But

$F^-{}_{(aq)} + H_3O^+{}_{(aq)} \leftrightarrows HF_{(aq)} + H_2O_{(l)}$

What is K_{eq} for this equilibrium?

$HF_{(aq)} + H_2O_{(l)} \leftrightarrows F^-{}_{(aq)} + H_3O^+{}_{(aq)}$ $K_a = 3.5 \times 10^{-4}$

Solving the problem requires a simultaneous solution of both equilibria

Problem: What is the solubility of MgF_2 in a solution that is 1M in HCl?

Since it is known that $[H^+] = 1.0M$ it will control the $[F^-]/[HF]$ which is involved in a weak acid equilibrium.

$$HF_{(aq)} + H_2O_{(l)} \leftrightarrows F^-_{(aq)} + H_3O^+_{(aq)} \quad K_a = 3.5 \times 10^{-4}$$

$$K_a = \frac{[H^+][F^-]}{[HF]} \rightarrow K_a/[H^+] = [F^-]/[HF] = 3.5 \times 10^{-4}$$

$$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2$$

$$MgF_{2\,(s)} \leftrightarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$$

At equil x y

Note: $y = [F^-]$ but x is the total amount that of MgF_2 dissolved and $2x = [F^-] + [HF]$, $y = 2x - [HF]$ and from above $[F^-] = [HF] \times 3.5 \times 10^{-4}$

$K_a/[H+] = [F\ ]/[HF] = 3.5 \times 10^{-4}$

$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2$

$$MgF_{2\,(s)} \leftrightarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$$

At equil x y = [F-]

Note: $y = [F^-]$ but 2x is the amount that of F dissolved, $2x = [F^-] + [HF]$, $y = 2x - [HF]$ and from above

$2x = [F^-] + [HF]$ therefore $[HF] = 2x\ [F^-]$

$y = [F^-] = [HF] \times 3.5 \times 10^{-4}$ Substitute from above

$y = [F^-] = (2x - [F-]) \times 3.5 \times 10^{-4}$ solving for [F-] we obtain

$[F^-] = 7.5 \times 10^{-4}x$

$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2 = (x)(7.5 \times 10^{-4}\,x)^2$

$= 5.63 \times 10^{-7}x^3 \rightarrow x = 5.08 \times 10^{-2}$

Review the Problem: What is the solubility of MgF_2 in a solution that is 1M in HCl?

$K_{sp} = 7.4 \times 10^{-11} = [Mg^{2+}][F^-]^2$

$MgF_{2\,(s)} \leftrightarrows Mg^{2+}_{(aq)} + 2F^-_{(aq)}$

At equil x y = [F-]

$X = 5.08 \times 10^{-2}\ M = [Mg^{2+}]$

and is the solubility of MgF_2 per liter in the presence of H^+ ion which affects the $[F^-]$ concentration through the weak acid equilibrium

$y = [F^-] = 7.5 \times 10^{-4}x$ and so $[F^-] = 3.8 \times 10^{-5}$ M

Remember that $K_a/[H^+] = [F-]/[HF] = 3.5 \times 10^{-4}$ and that $[HF] = 2x - [F^-]$ this should check out

$[HF] = 2x - [F^-] = 1.016 \times 10^{-1} – 3.8 \times 10^{-5} = 0.1016$ M

$[F^-]/[HF] = 3.8 \times 10^{-5} / 0.1016 = 3.7 \times 10^{-4}$ ✓(very close)

Multiple solubility and Selective Precipitation

Consider AgCl, AgBr, and AgI solubility

$K_{sp} = 1.8 \times 10^{-10}$ $\mathbf{AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}}$

$K_{sp} = 5.4 \times 10^{-13}$ $\mathbf{AgBr_{(s)} \leftrightarrows Ag^+_{(aq)} + Br^-_{(aq)}}$

$K_{sp} = 8.5 \times 10^{-17}$ $\mathbf{AgI_{(s)} \leftrightarrows Ag^+_{(aq)} + I^-_{(aq)}}$

Problem:

If a solution contains the three ions Cl^-, Br^-, and I^- in equal concentrations of 0.1 M at what concentration of added Ag^+ will each of the halides just begin to ion precipitate?

If a solution contains the three ions Cl^- ,Br^- ,and I^- in equal concentrations of 0.1 M at what concentration of added will each ion precipitate?

Since AgI has the smallest K_{sp} it is least soluble

$K_{sp} = 8.5 \times 10^{-17}$ $AgI_{(s)} \leftrightarrows Ag^+_{(aq)} + I^-_{(aq)}$

Since $[I^-] = 0.1$ M

The $[Ag^+] = K_{sp}/0.1 = 8.5 \times 10^{-16}$M at the point when AgI begins to ppt.

$[Ag^+] = 8.5 \times 10^{-16}$M

AgBr will begin to ppt when $[Ag^+] = K_{sp}/0.1$

$[Ag^+] = 5.4 \times 10^{-12}$M

AgCl will begin to ppt when $[Ag^+] = K_{sp}/0.1$

$[Ag^+] = 1.8 \times 10^{-9}$ M

Problem: What volume of 1.0 M $AgNO_3$ will be required to cause the precipitation of the salts AgI, AgBr, and AgCl in a 25 mL solution of these ions if Cl^-, Br^-, and I^- are all present in equal concentrations of 0.1 M? What is the concentration of each ion remaining in solution when the next ion begins to precipitate? When I- first ppts

$[Ag^+] = 8.5 \times 10^{-16}M = V_{Ag} \times 1.0M/V_t = V_{Ag} \times 1.0M/(V_i + V_{Ag})$ but V_{Ag} is small

So $V_{Ag} = 8.5 \times 10^{-16}M \times V_i = 2.1 \times 10^{-17}$ Liters

We know that $[Ag^+] = 5.4 \times 10^{-12}$M when AgBr begins to precipitate.

Therefore, since $K_{sp} = 8.5 \times 10^{-17}$ for AgI

the $[I^-]_f = K_{spAgI}/[Ag^+] = 1.57 \times 10^{-5}$M

The mole of $[I^-]_f$ = (initial moles I^- - moles precipated)/V

since $[AgNO_3]$ is large we will neglect any change in volume during the rxn as a first approximation

$[I^-]_f = 1.57 \times 10^{-5}$M = (0.025 x 0.1 - moles precipated)/0.025

Mole I^- precipitated = $0.025(0.1) – (0.025)(1.57 \times 10^{-5})$

$= 2.49 \times 10^{-3}$ mole I- precipitated

Mole I^- precipitated = (0.025)(0.1) – (0.025)(1.57 x 10^{-5})
= 2.49 x 10^{-3} mole I^- precipitated

since $[Ag^+]$ = 1.0 M and we consumed 2.5 x 10^{-3} mole the volume of Ag solution added when Br^- just begins to ppt

= 2.5 x10^{-3}mole/1.0M = 2.5 mL

We could now use this to correct our V above to 27.5 ml and recalculate the mole precipitated. The results are not significantly affected.

Repeating the procedure when AgCl first precipitates we find,
(correcting for the fact that the $[Cl^-]$ is now 0.09 M due to the slight dilution of adding 2.5 mL of Ag^+ solution) that
$[Ag^+] = K_{spAgCl}/ [Cl^-]$ = 1.8 x 10^{-10} /0.09
= 1.98x 10^{-9}M
Therefore since, K_{sp} = 5.4 x 10^{-13} for AgBr
The $[Br^-]_f = K_{spAgBr}/ [Ag+]$ = 2.72 x 10^{-4} M

The mole of $[Br^-]_f$ = (initial moles Br^- - moles precipated)/V
since $[AgNO_3]$ is large we will again neglect any change in volume as a first approximation

We know that $[Br^-]_f$ = 2.72 x 10^{-4} M when AgCl begins to precipitate.

$[Br^-]_f$ = 2.72 x 10^{-4} M = (0.025 x 0.1 - moles precipated)/0.0275
Mole Br^- precipitated = (0.025)(0.1) – (0.0275)(2.72 x 10^{-4})

= 2.49 x 10^{-3} mole Br^- precipitated

since $[Ag^+]$ = 1.0 M and we consumed 2.5 x 10^{-3} mole the volume of Ag solution added when Cl^- just begins to ppt
= 2.5 x10^{-3}mole/1.0M = 2.5 mL additional

Total $AgNO_3$ added is now 5.0 ml
We could now use this to correct our V above to 30.0 ml and recalculate the mole precipitated. The results are not significantly affected.
It is clear that an additional 2.5 mL will precipitate all Cl^-

Summary of sequential precipitation of I^-, Cl^-, Br^-

We find that 2.49×10^{-3} mole ppt before the next ion begins to ppt and that the reaction is so favorable that essentially all added Ag^+ ppts

2.49×10^{-3} ppt/2.5×10^{-3} initial present

→ 99.6% halide precipitated

The ions can be sequentially separated by slow addition of Ag^+ ion

Formation of Complex Ions

Formation of Complex ions can be favorable between a Lewis base and a transition metal cation – This can affect solubility of ions

$Cu^{2+} + 4\,NH_3 \leftrightarrows [Cu(NH_3)_4]^{2+}$ $\quad K_f = \dfrac{[Cu(NH_3)_4]}{[Cu^{2+}][NH_3]^4}$

$K_f = 5.6 \times 10^{11}$

$Ag^+ + 2NH_3 \leftrightarrows [Ag(NH_3)_2]^{1+}$ $\quad K_f = \dfrac{[Ag(NH_3)_4]}{[Ag^{1+}][NH_3]^2}$

$K_f = 1.7 \times 10^7$

Solubility of Ag^+ in the presence of NH_3

$AgCl_{(s)} \leftrightarrows Ag^+_{(aq)} + Cl^-_{(aq)}$ $\quad K_{sp} = [Ag^+][Cl^-] = 1.8 \times 10^{-10}$

$Ag^+ + 2NH_3 \leftrightarrows [Ag(NH_3)_2]^{1+}$ $\quad K_f = \dfrac{[Ag(NH_3)_4]}{[Ag^{1+}][NH_3]^2} = 1.7 \times 10^7$

Overall

$$AgCl_{(s)} + 2NH_3 \leftrightarrows [Ag(NH_3)_2]^{1+} + Cl\text{-}_{(aq)}$$

$$K_O = \frac{[Cl^-][Ag(NH_3)_4]}{[Ag(NH_3)_2]} = K_{sp} \times K_f$$

$$K_O = 3.1 \times 10^{-3}$$

Solubility of Ag^+ in the presence of NH_3

$AgCl_{(s)} + 2NH_3 \leftrightarrows [Ag(NH_3)_2]^{1+} + Cl^-_{(aq)}$ $K_O = \frac{[Cl^-][Ag(NH_3)_4]}{[NH_3]^2}$

$K_O = 3.1 \times 10^{-3}$

Problem: What is the solubility of AgCl in a 3.0M solution of NH_3?

	$AgCl_{(s)}$ +	$2NH_3$ $\leftrightarrows$	$[Ag(NH_3)_2]^{1+}$ +	$Cl^-_{(aq)}$
Initial		3.0	0	0
Equil		3-x	x	x

$K_O = \frac{[Cl^-][Ag(NH_3)_4]}{[NH_3]^2} = 3.1 \times 10^{-3} = (x)(x)/(3-x)^2 = x^2/(3-x)^2$

$x/(3-x) = (3.1 \times 10^{-3})^{1/2}$ $x = 0.167M$ $x << 3$ ☑

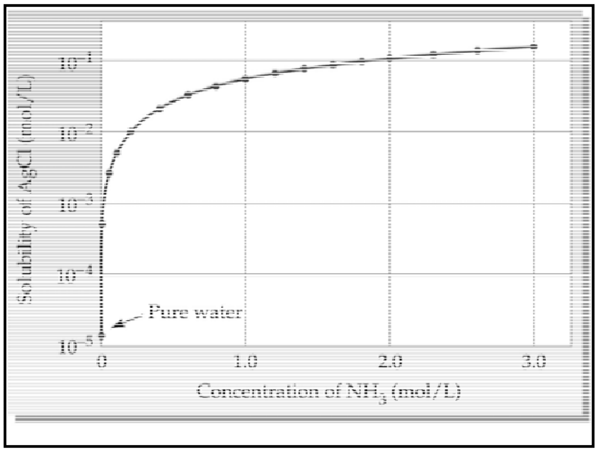
Solubility of Ag^+ in the presence of NH_3

Problem: What is the solubility of AgCl in a 3.0M solution of NH_3?

$[Ag(NH_3)_2]^{1+} = 0.167M$ at equilibrium

So, 0.167 mole of AgCl dissolve per liter

This is compared to 1.3×10^{-5} mole in water alone!

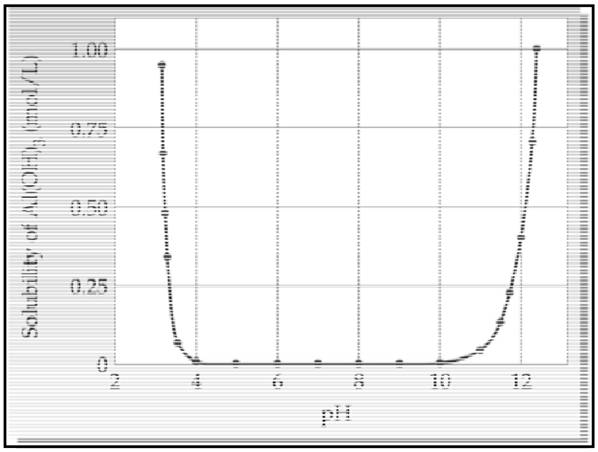


Amphoteric behavior of Al^{3+}

Some ions are *Amphoteric* and are soluble in the presence of either base or acid but not in neutral solution

$Al(OH)_{3\,(s)} + 3H^{+}_{(aq)} \leftrightarrows Al^{3+}_{(aq)} + 3H_2O_{(l)}$

$Al(OH)_{3\,(s)} + OH^{-}_{(aq)} \leftrightarrows Al(OH)_4{}^{3+}_{(aq)}$



Hard Water a Practical problem involving solubility

- $CaCO_3$ is the principle salt in water in So. FL

Usually our water is saturated at room temp

At elevated temperature the following equilibria occur

$$2HCO_3^{-} \leftrightarrows CO_{2\,(g)} + CO_3^{-}$$

$$Ca^{2+} + CO_3^{-} \leftrightarrows CaCO_{3\,(s)}$$

The result is that unsoftened water when heat produces solid calcite in water heaters and pipes