Equilibri acido-base ed equilibri di solubilità

Capitolo 16



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).

$$CH_{3}COONa (s) \longrightarrow Na^{+} (aq) + CH_{3}COO^{-} (aq)$$

$$common$$

$$CH_{3}COOH (aq) \longrightarrow H^{+} (aq) + CH_{3}COO^{-} (aq)$$
ion

Consider mixture of salt NaA and weak acid HA.

NaA (s) Na⁺ (aq) + A⁻ (aq)
HA (aq) H⁺ (aq) + A⁻ (aq)

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

$$[H^+] = -\log K_a - \log \frac{[HA]}{[A^-]}$$
Henderson-Hasselbalch
equation
H = pK_a + log \frac{[A^-]}{[HA]}
$$PH = pK_a + \log \frac{[A^-]}{[HA]}$$

$$pK_a = -\log K_a$$



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)	← H ⁺ (aq)	+ HCOO ⁻ (aq)
Initial (M)	0.30	0.00	0.52
Change (M)	-X	+ <i>X</i>	+ <i>x</i>
Equilibrium (M)	0.30 - <i>x</i>	X	0.52 + <i>x</i>
Common ion effect 0.30 − <i>x</i> ≈ 0.30 0.52 + <i>x</i> ≈ 0.52	pH = p K_a + log $\frac{[\text{HCOO}^-]}{[\text{HCOOH}]}$ pH = 3.77 + log $\frac{[0.52]}{[0.30]}$ = 4.01		$\frac{300^{-}]}{00H]}$ $\frac{32}{0} = 4.01$
HCOOH p <i>K_a</i> = 3.77			

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 CH₃COOH and CH₃COONa

Add strong acid $H^+(aq) + CH_3COO^-(aq) \longrightarrow CH_3COOH(aq)$ Add strong base $OH^-(aq) + CH_3COOH(aq) \longrightarrow CH_3COO^-(aq) + H_2O(l)$

HCI
$$\longrightarrow$$
 H⁺ + Cl⁻
HCI + CH₃COO⁻ \longrightarrow CH₃COOH + Cl⁻





(a) KF 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 NH₃/0.36 M NH₄Cl 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?

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

pH = p
$$K_a$$
 + log $\frac{[NH_3]}{[NH_4^+]}$ p K_a = 9.25 pH = 9.25 + log $\frac{[0.30]}{[0.36]}$ = 9.17

start (moles)0.0290.0010.024 $NH_4^+(aq) + OH^-(aq) \longrightarrow H_2O(l) + NH_3(aq)$ end (moles)0.0280.00.025

final volume = 80.0 mL + 20.0 mL = 100 mL

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

Chemistry In Action: Maintaining the pH of Blood



Titrations

In a *titration* a solution of accurately known concentration is added gradually added 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



Strong Acid-Strong Base Titrations

NaOH (aq) + HCl (aq) \longrightarrow H₂O (*l*) + NaCl (aq) OH⁻ (aq) + H⁺ (aq) \longrightarrow H₂O (*l*)



Weak Acid-Strong Base Titrations

CH₃COOH (*aq*) + NaOH (*aq*) → CH₃COONa (*aq*) + H₂O (*l*) CH₃COOH (*aq*) + OH⁻ (*aq*) → CH₃COO⁻ (*aq*) + H₂O (*l*) At equivalence point (pH > 7):

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



Strong Acid-Weak Base Titrations

 $\begin{array}{l} \mathsf{HCI} (aq) + \mathsf{NH}_3 (aq) \longrightarrow \mathsf{NH}_4 \mathsf{CI} (aq) \\ \mathsf{H}^+ (aq) + \mathsf{NH}_3 (aq) \longrightarrow \mathsf{NH}_4 \mathsf{CI} (aq) \end{array}$

At equivalence point (pH < 7):

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



Exactly 100 mL of 0.10 M HNO₂ are titrated with a 0.10 M NaOH solution. What is the pH at the equivalence point? start (moles) 0.01 0.01 $HNO_2(aq) + OH^-(aq) \longrightarrow NO_2^-(aq) + H_2O(l)$ 0.0 end (moles) 0.0 0.01 $[NO_2^{-}] = \frac{0.01}{0.200} = 0.05 M$ Final volume = 200 mL $NO_2^-(aq) + H_2O(l) \longrightarrow OH^-(aq) + HNO_2(aq)$ Initial (M) 0.00 0.05 0.00 Change (*M*) +x-X +xEquilibrium (M) 0.05 - xX X $K_b = \frac{[OH^-][HNO_2]}{[NO_2^-]} = \frac{x^2}{0.05 - x} = 2.2 \times 10^{-11} \text{ pOH} = 5.98$ pH = 14 - pOH = 8.02 $0.05 - x \approx 0.05$ $x \approx 1.05 \times 10^{-6} = [OH^{-1}]$

Acid-Base Indicators

$$\begin{array}{l} \text{HIn } (aq) & \longrightarrow \\ \hline \text{HIn} \\ \hline [\text{HIn}] \\ \hline [\text{In}^{-}] \end{array} & \geq 10 \quad \text{Color of acid (HIn) predominates} \\ \hline [\text{HIn}] \\ \hline [\text{In}^{-}] \end{array} & \leq 10 \quad \text{Color of conjugate base (In}^{-}) \text{ predominates} \end{array}$$

TABLE 16.1	E 16.1 Some Common Acid-Base Indicators			
Color				
Indicator		In Acid	In Base	pH Range*
Thymol blue		Red	Yellow	1.2-2.8
Bromophenol	blue	Yellow	Bluish purple	3.0-4.6
Methyl orang	e	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
Phenolphthale	ein	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.

Solutions of Cabbage



рΗ

->

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



17.5



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 C	ommon Acid-Base	Indicators	
	Color			
Indicator		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	e	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
Phenolphthale	in	Colorless	Reddish pink	8.3-10.0
Phenolphthale	in fined as the ra	Colorless	Reddish pink	8.3-10.0

Solubility Equilibria

AgCl (s)
$$\longrightarrow$$
 Ag⁺ (aq) + Cl⁻ (aq)

 $K_{sp} = [Ag^+][CI^-]$ K_{sp} is the solubility product constant

 $MgF_{2} (s) \rightleftharpoons Mg^{2+} (aq) + 2F^{-} (aq) \qquad K_{sp} = [Mg^{2+}][F^{-}]^{2}$ $Ag_{2}CO_{3} (s) \rightleftharpoons 2Ag^{+} (aq) + CO_{3}^{2-} (aq) \qquad K_{sp} = [Ag^{+}]^{2}[CO_{3}^{2-}]$ $Ca_{3}(PO_{4})_{2} (s) \rightleftharpoons 3Ca^{2+} (aq) + 2PO_{4}^{3-} (aq) \qquad K_{sp} = [Ca^{2+}]^{3}[PO_{4}^{3-}]^{2}$

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

TABLE 16.2 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 (BaCO3)	8.1×10^{-9}	Lead(II) fluoride (PbF ₂)	4.1×10^{-8}
Barium fluoride (BaF2)	1.7×10^{-6}	Lead(II) iodide (PbI2)	1.4×10^{-8}
Barium sulfate (BaSO ₄)	1.1×10^{-10}	Lead(II) sulfide (PbS)	3.4×10^{-28}
Bismuth sulfide (Bi2S3)	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 (CaCO3)	8.7×10^{-9}	Manganese(II) sulfide (MnS)	3.0×10^{-14}
Calcium fluoride (CaF2)	4.0×10^{-11}	Mercury(I) chloride (Hg2Cl2)	3.5×10^{-18}
Calcium hydroxide [Ca(OH)2]	8.0×10^{-6}	Mercury(II) sulfide (HgS)	4.0×10^{-54}
Calcium phosphate [Ca3(PO4)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 ₂ CO 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 ₂ SO ₄)	1.4×10^{-5}
Copper(II) sulfide (CuS)	6.0×10^{-37}	Silver sulfide (Ag ₂ S)	6.0×10^{-51}
Iron(II) hydroxide [Fe(OH)2]	1.6×10^{-14}	Strontium carbonate (SrCO3)	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.





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

 Initial (M)
 0.00
 0.00
 $K_{sp} = [Ag^+][Cl^-]$

 Change (M)
 +s
 +s
 $K_{sp} = s^2$

 Equilibrium (M)
 s
 s
 s = $\sqrt{K_{sp}}$

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

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

TABLE 16.3	Relationship Between $K_{\rm sp}$	and Molar Solul	bility (s)	
Compound	K _{sp} Expression	Cation	Anion	Relation Between K_{sp} and s
AgCl BaSO4	[Ag ⁺][Cl ⁻] [Ba ²⁺][SO ₄ ²⁻]	\$ \$	S S	$K_{\rm sp} = s^2; s = (K_{\rm sp})^{\frac{1}{2}}$ $K_{\rm sp} = s^2; s = (K_{\rm sp})^{\frac{1}{2}}$
Ag ₂ CO ₃	[Ag ⁺] ² [CO ₃ ²⁻]	2 <i>s</i>	\$	$K_{\rm sp} = 4s^3; s = a \frac{K_{\rm sp}}{4} b^{\frac{1}{3}}$
PbF ₂	$[Pb^{2+}][F^{-}]^{2}$	S	2 <i>s</i>	$K_{\rm sp} = 4s^3; s = a \frac{K_{\rm sp}}{4} b^{\frac{1}{3}}$
Al(OH) ₃	[Al ³⁺][OH ⁻] ³	S	35	$K_{\rm sp} = 27s^4; s = a \frac{K_{\rm sp}}{27} b^4$
Ca ₃ (PO ₄) ₂	$[Ca^{2+}]^{3}[PO_{4}^{3-}]^{2}$	35	2 <i>s</i>	$K_{\rm sp} = 108s^5; s = a \frac{K_{\rm sp}}{108} b^{\frac{1}{5}}$



The ions present in solution are Na⁺, OH⁻, Ca²⁺, Cl⁻.

Only possible precipitate is Ca(OH)₂ (solubility rules).

Is $Q > K_{sp}$ for Ca(OH)₂?

 $[Ca^{2+}]_0 = 0.100 M$ $[OH^-]_0 = 4.0 \times 10^{-4} M$ $Q = [Ca^{2+}]_0 [OH^-]_0^2 = 0.10 \times (4.0 \times 10^{-4})^2 = 1.6 \times 10^{-8}$ $K_{sp} = [Ca^{2+}][OH^-]^2 = 8.0 \times 10^{-6}$ $Q < K_{sp}$ 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)
$$\longrightarrow$$
 Ag⁺ (aq) + Br⁻ (aq) $K_{sp} = 7.7 \times 10^{-13}$
 $K_{sp} = [Ag^+][Br^-]$

$$[Ag^+] = \frac{K_{sp}}{[Br^-]} = \frac{7.7 \times 10^{-13}}{0.020} = 3.9 \times 10^{-11} M$$
AgCl (s) \longrightarrow Ag⁺ (aq) + Cl⁻ (aq) $K_{sp} = 1.6 \times 10^{-10}$
 $K_{sp} = [Ag^+][Cl^-]$

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

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

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?

AgBr (s)
$$\overrightarrow{}$$
 Ag⁺ (aq) + Br⁻ (aq)
 $K_{sp} = 7.7 \times 10^{-13}$
 $s^2 = K_{sp}$
 $s = 8.8 \times 10^{-7}$

NaBr (s)
$$\longrightarrow$$
 Na⁺ (aq) + Br⁻ (aq)
[Br⁻] = 0.0010 M
AgBr (s) \longrightarrow Ag⁺ (aq) + Br⁻ (aq)
[Ag⁺] = s
[Br⁻] = 0.0010 + s \approx 0.0010
 $K_{sp} = 0.0010 \times s$
 $s = 7.7 \times 10^{-10}$

pH and Solubility



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

Decrease solubility of Mg(

- Insoluble bases dissolve in acidic solutions
- Insoluble acids dissolve in basic solutions

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

$$K_{sp} = [Mg^{2+}][OH^{-}]^2 = 1.2 \times 10^{-11}$$
At pH less than 10.45 $K_{sp} = (s)(2s)^2 = 4s^3$ Lower [OH^-] $4s^3 = 1.2 \times 10^{-11}$ $OH^- (aq) + H^+ (aq) \longrightarrow H_2O (l)$ $s = 1.4 \times 10^{-4} M$ Increase solubility of Mg(OH)₂ $[OH^-] = 2s = 2.8 \times 10^{-4} M$ At pH greater than 10.45 $pOH = 3.55 \ pH = 10.45$ Raise [OH^-]

17.9

Complex Ion Equilibria and Solubility

A *complex ion* is an ion containing a central metal cation bonded to one or more molecules or ions.

$$Co^{2+}(aq) + 4Cl^{-}(aq) \longleftarrow CoCl_{4}^{2-}(aq)$$

The *formation constant or stability constant* (K_f) is the equilibrium constant for the complex ion formation.

$$\mathcal{K}_{f} = \frac{\left[\operatorname{CoCl}_{4}^{2^{-}}\right]}{\left[\operatorname{Co}^{2^{+}}\right]\left[\operatorname{Cl}^{-}\right]^{4}}$$

$$\mathcal{K}_{f} \uparrow \qquad \text{stability of complex} \uparrow$$



TABLE 16.4

Formation Constants of Selected Complex Ions in Water at 25°C

Complex Ion	Equilibrium Expression	Formation Constant (K _f)	
$Ag(NH_3)_2^+$	$Ag^+ + 2NH_3 \implies Ag(NH_3)_2^+$	1.5×10^{7}	
$Ag(CN)_2^-$	$Ag^+ + 2CN^- \Longrightarrow Ag(CN)_2^-$	1.0×10^{21}	
$Cu(CN)_4^{2-}$	$Cu^{2+} + 4CN^{-} \Longrightarrow Cu(CN)_4^{2-}$	1.0×10^{25}	
$Cu(NH_3)_4^{2+}$	$Cu^{2+} + 4NH_3 \Longrightarrow Cu(NH_3)_4^{2+}$	5.0×10^{13}	
$Cd(CN)_4^{2-}$	$Cd^{2+} + 4CN^{-} \Longrightarrow Cd(CN)_4^{2-}$	7.1×10^{16}	
CdI_4^{2-}	$Cd^{2+} + 4I^- \Longrightarrow CdI_4^{2-}$	2.0×10^{6}	
$HgCl_4^{2-}$	$Hg^{2+} + 4Cl^- \Longrightarrow HgCl_4^{2-}$	1.7×10^{16}	
HgI_4^{2-}	$Hg^{2+} + 4I^- \Longrightarrow HgI_4^{2-}$	2.0×10^{30}	
$Hg(CN)_4^{2-}$	$Hg^{2+} + 4CN^{-} \Longrightarrow Hg(CN)_4^{2-}$	2.5×10^{41}	
$Co(NH_3)_6^{3+}$	$Co^{3+} + 6NH_3 \Longrightarrow Co(NH_3)_6^{3+}$	5.0×10^{31}	
$Zn(NH_3)_4^{2+}$	$Zn^{2+} + 4NH_3 \implies Zn(NH_3)_4^{2+}$	2.9×10^{9}	

TABLE 16.5 Separation of Cations into Groups According to Their Precipitation Reactions with Various Reagents

Group	Cation	Precipitating Reagents	Insoluble Compound	K _{sp}
1	Ag ⁺	HCl	AgCl	1.6×10^{-10}
	Hg_{2}^{2+}		Hg ₂ Cl ₂	3.5×10^{-18}
	Pb^{2+}	Ļ	PbCl ₂	2.4×10^{-4}
2	Bi ³⁺	H ₂ S	Bi ₂ S ₃	1.6×10^{-72}
	Cd ²⁺	in acidic	CdS	8.0×10^{-28}
	Cu ²⁺	solutions	CuS	6.0×10^{-37}
	Hg ²⁺		HgS	4.0×10^{-54}
	Sn ²⁺	Ļ	SnS	1.0×10^{-26}
3	Al ³⁺	H ₂ S	Al(OH) ₃	1.8×10^{-33}
	Co ²⁺	in basic	CoS	4.0×10^{-21}
	Cr ³⁺	solutions	Cr(OH) ₃	3.0×10^{-29}
	Fe ²⁺		FeS	6.0×10^{-19}
	Mn ²⁺		MnS	3.0×10^{-14}
	Ni ²⁺		NiS	1.4×10^{-24}
	Zn^{2+}	Ļ	ZnS	3.0×10^{-23}
4	Ba ²⁺	Na ₂ CO ₃	BaCO ₃	8.1×10^{-9}
	Ca ²⁺		CaCO ₃	8.7×10^{-9}
	Sr ²⁺	Ļ	SrCO ₃	1.6×10^{-9}
5	K ⁺	No precipitating	None	
	Na ⁺	reagent	None	
	NH_4^+		None	
	-			17.11





Qualitative Analysis of Cations



Flame Test for Cations



lithium

sodium

potassium

copper



Chemistry In Action: How an Eggshell is Formed



$$Ca^{2+}(aq) + CO_3^{2-}(aq) \longrightarrow CaCO_3(s)$$

 $CO_2(g) + H_2O(I) \xrightarrow[anhydrase]{carbonic} H_2CO_3(aq)$

$$H_2CO_3(aq) \longrightarrow H^+(aq) + HCO_3^-(aq)$$

$$HCO_{3^{-}}(aq) \rightleftharpoons H^{+}(aq) + CO_{3^{2-}}(aq)$$