Acid-Base Equilibria and Solubility Equilibria

Chapter 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).

$$CH_3COONa\ (s) \longrightarrow Na^+\ (aq) + CH_3COO^-\ (aq)$$

$$CH_3COOH\ (aq) \rightleftharpoons H^+\ (aq) + CH_3COO^-\ (aq)$$

common ion

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Consider mixture of salt NaA and weak acid HA.

$NaA\ (s) \rightarrow Na^+\ (aq) + A^-\ (aq)$

$HA\ (aq) \rightleftharpoons H^+\ (aq) + A^-\ (aq)$

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

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

Henderson-Hasselbalch equation

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

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

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

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

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

Mixture of weak acid and conjugate base!

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

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 $pK_a = 3.77$

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

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

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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

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

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Which of the following are buffer systems? (a) KF/HF (b) KBr/HBr, (c) Na_2CO_3/$NaHCO_3$

(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

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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?

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

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

	NH_4^+	OH^-	H_2O	NH_3
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

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

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Solubility Equilibria

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

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

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

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

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

<u>Dissolution of an ionic solid in aqueous solution:</u>

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

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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 ($BaCO_3$)	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}

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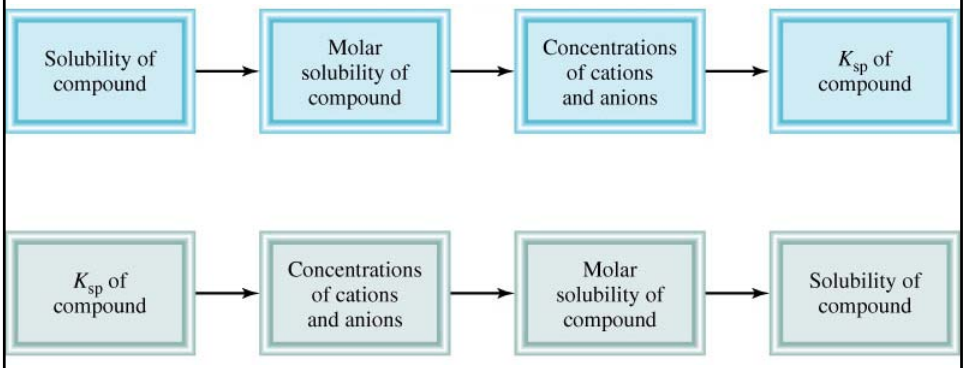
Molar solubility (mol/L) is the number of moles of solute dissolved in 1 L of a saturated solution.

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



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

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

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

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

$K_{sp} = s^2$

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

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

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

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

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TABLE 16.3 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	$[Ag^+]^2[CO_3^{2-}]$	2*s*	*s*	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
PbF_2	$[Pb^{2+}][F^-]^2$	*s*	2*s*	$K_{sp} = 4s^3;\ s = \left(\frac{K_{sp}}{4}\right)^{\frac{1}{3}}$
$Al(OH)_3$	$[Al^{3+}][OH^-]^3$	*s*	3*s*	$K_{sp} = 27s^4;\ s = \left(\frac{K_{sp}}{27}\right)^{\frac{1}{4}}$
$Ca_3(PO_4)_2$	$[Ca^{2+}]^3[PO_4^{3-}]^2$	3*s*	2*s*	$K_{sp} = 108s^5;\ s = \left(\frac{K_{sp}}{108}\right)^{\frac{1}{5}}$

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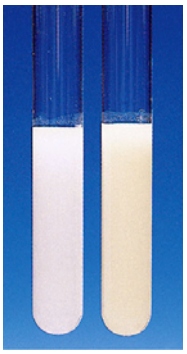
What concentration of Ag is required to precipitate ONLY AgBr in a solution that contains both Br^- and Cl^- at a concentration of 0.02 *M*?

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

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

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



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

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

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

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

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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?

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

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

$s^2 = K_{sp}$

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

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

$[Br^-] = 0.0010\ M$

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

$[Ag^+] = s$

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

$K_{sp} = 0.0010 \times s$

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

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