

# Chapter 9

## Aqueous Solutions and Chemical Equilibria

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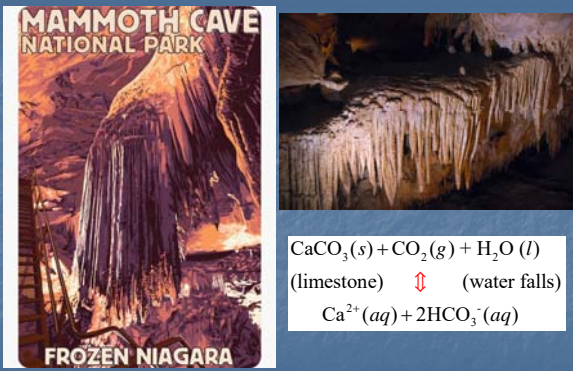
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$\text{CaCO}_3(s) + \text{CO}_2(g) + \text{H}_2\text{O}(l)$   
(limestone)  $\rightleftharpoons$  (water falls)  
 $\text{Ca}^{2+}(aq) + 2\text{HCO}_3^-(aq)$

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### Classifying Solutions of Electrolytes

- Electrolytes—solutes form ions when dissolved in water (or certain other solvents, e.g. acetonitrile)
- Strong (weak, non-) electrolytes

$\text{HNO}_3 + \text{H}_2\text{O} \rightarrow \text{NO}_3^- + \text{H}_3\text{O}^+$  (completely ionized)  
 $\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{CH}_3\text{COO}^- + \text{H}_3\text{O}^+$  (partially ionized)  
sugar (s) + water = sugar aqueous soln (completely non-ionized)

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TABLE 9-1

Classification of Electrolytes	
Strong	Weak HF
1. Inorganic acids such as HNO <sub>3</sub> , HClO <sub>4</sub> , H <sub>2</sub> SO <sub>4</sub> , HCl, HI, HBr, HClO <sub>3</sub> , HBrO <sub>3</sub>	1. Many inorganic acids, including H <sub>2</sub> CO <sub>3</sub> , H <sub>3</sub> BO <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> , H <sub>2</sub> S, H <sub>2</sub> SO <sub>3</sub>
2. Alkali and alkaline-earth hydroxides	2. Most organic acids
3. Most salts	3. Ammonia and most organic bases
	4. Halides, cyanides, and thiocyanates of Hg, Zn, and Cd

\*H<sub>2</sub>SO<sub>4</sub> is completely dissociated into HSO<sub>4</sub><sup>-</sup> and H<sub>3</sub>O<sup>+</sup> ions and for this reason is classified as a strong electrolyte. It should be noted, however, that the HSO<sub>4</sub><sup>-</sup> ion is a weak electrolyte, being only partially dissociated into SO<sub>4</sub><sup>2-</sup> and H<sub>3</sub>O<sup>+</sup>.

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Ca(OH)<sub>2</sub> → Ca<sup>2+</sup> + 2OH<sup>-</sup>, no Ca(OH)<sup>-</sup> in solution  
HF is a weak electrolyte due to hydrogen bond.

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## Acids and Bases

- An acid donates protons, a base accepts protons
- An acid donates protons only in the presence of a proton acceptor (a base). A base accepts protons only in the presence of a proton donor (an acid)

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## Bronsted-Lowry Acids and Bases

These two chemists pointed out that acids and bases can be seen as **proton transfer reactions**.

According to the Bronsted-Lowry concept:

- An acid donates a proton and the base accepts it.
- Newly formed species are called conjugate base and conjugate acid, respectively.

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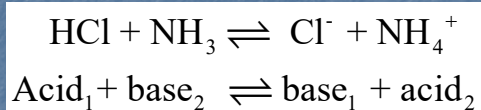
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acid + base  $\rightleftharpoons$  conjugate base + conjugate acid



A conjugate base is formed when an acid loses a proton ( $\text{HCl} \rightarrow \text{Cl}^-$ ); A conjugate acid is formed when a base accepts a proton ( $\text{NH}_3 \rightarrow \text{NH}_4^+$ )

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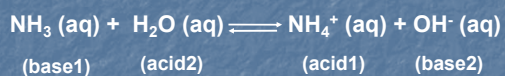
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Consider the reaction of  $\text{NH}_3$  with  $\text{H}_2\text{O}$ :



Note:

$\text{NH}_3$  &  $\text{NH}_4^+$  are a conjugate acid-base pair.

$\text{H}_2\text{O}$  &  $\text{OH}^-$  also a conjugate acid-base pair

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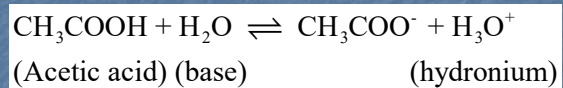
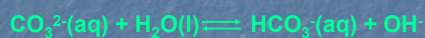
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### Example

Identify the acid and base species in the following equations:



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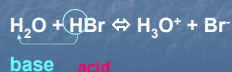
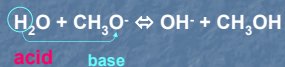
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### Amphiprotic species ("amphi-": both):

a species that can act as either an acid or a base, depending on the other reactant.

Consider water:



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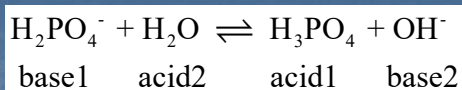
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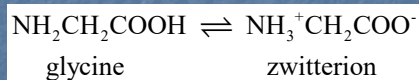
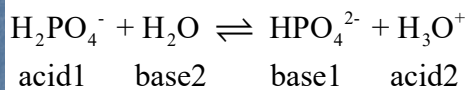
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(amphiprotic)



"sweetener"

A zwitterion is an ion that bears both a positive and a negative charge

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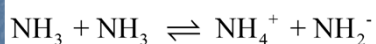
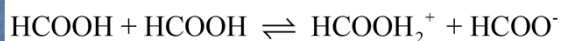
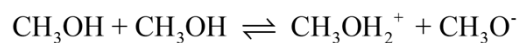
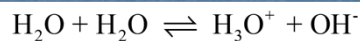
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### AUTOPROTOLYSIS

In autoprotolysis a proton is transferred between two identical molecules, one of which acts as a Brønsted acid, releasing a proton which is accepted by the other molecule acting as a Brønsted base.



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## AUTOPROTOLYSIS

Water undergoes self-ionization → **autoprotolysis**, since  $\text{H}_2\text{O}$  acts as an acid and a base.



The extent of autoprotolysis is very **small**.

The **equilibrium constant** expression for this reaction is:

$$K_c = \frac{[\text{H}_3\text{O}^+][\text{OH}^-]}{[\text{H}_2\text{O}]^2}$$

The concentration of water is essentially constant.

Therefore:  $\underbrace{[\text{H}_2\text{O}]^2}_{\text{constant}} K_c = [\text{H}_3\text{O}^+][\text{OH}^-]$   
 $\text{constant} = K_w$

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TABLE 9-3

Variation of  $K_w$  with Temperature

Temperature, °C	$K_w$
0	$0.114 \times 10^{-14}$
25	$1.01 \times 10^{-14}$
50	$5.47 \times 10^{-14}$
75	$19.9 \times 10^{-14}$
100	$49 \times 10^{-14}$

Example: Calculate the hydronium and hydroxide ion concentration of pure water at 25 °C and 100 °C.

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We call the equilibrium value of the ion product  $[\text{H}_3\text{O}^+][\text{OH}^-]$  the **ion-product constant** of water.

$$K_w = [\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14} \text{ at } 25^\circ\text{C}$$

Using  $K_w$  you can calculate concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in pure water.

$$[\text{H}_3\text{O}^+][\text{OH}^-] = 1.0 \times 10^{-14}$$

But  $[\text{H}_3\text{O}^+] = [\text{OH}^-]$  in pure water

$$\therefore [\text{H}_3\text{O}^+] = [\text{OH}^-] = 1.0 \times 10^{-7} \text{ M}$$

If you **add an acid or a base** to water the concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  will no longer be equal. But  $K_w$  will still hold.

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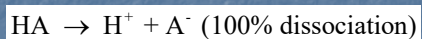
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## Acid / Base Strengths

- The strength of an acid or base is determined by the extent it dissociates in water to form  $H^+$  or  $OH^-$  respectively

- Strong acids:



$$[H^+] = [HA]_{\text{initial}}$$

- Strong bases:



$$[OH^-] = [MOH]_{\text{initial}}$$

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## Weak Acid

- Weak acids only partially dissociate to give  $H^+$  in  $H_2O$

- Equilibrium Constant  
 $HA + H_2O \rightleftharpoons H_3O^+ + A^-$

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

$K_a$  = acid dissociation constant

- The smaller the  $K_a$  value, the weaker the acid

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## Weak Base

- Weak bases react with water by abstracting a proton

- Equilibrium Constant  
 $B + H_2O \rightleftharpoons BH^+ + OH^-$

$$K_b = \frac{[BH^+][OH^-]}{[B]}$$

$K_b$  = base hydrolysis constant

Hydrolysis = reaction with water

- The smaller the  $K_b$  value, the weaker the base

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Strongest acid	$\text{HClO}_4 + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{ClO}_4^-$ $\text{HCl} + \text{H}_2\text{O} \longrightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$ $\text{H}_3\text{PO}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{H}_2\text{PO}_4^-$ $\text{Al}(\text{H}_2\text{O})_6^{3+} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{AlOH}(\text{H}_2\text{O})_5^{2+}$ $\text{HC}_2\text{H}_3\text{O}_2 + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{C}_2\text{H}_3\text{O}_2^-$ $\text{H}_2\text{PO}_4^- + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{HPO}_4^{2-}$ $\text{NH}_4^+ + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{NH}_3$	Weakest base
Weakest acid		Strongest base

• The strongest acids have the weakest conjugate bases and the strongest bases have the weakest conjugate acids.  
 • A acid (base) can be cationic, anionic, neutral.

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### Differentiating/Leveling Solvents

- In water, perchloric and hydrochloric acids are strong acids and have the same strength.
- In acetic acid, perchloric acid is considerably stronger than HCl; its dissociation being ~5000 times greater.
- Acetic acid acts as *differentiating solvent* toward the two acids by revealing the inherent differences in their activities, and water is called *leveling solvent* for perchloric, hydrochloric (and nitric) acids because all three are 100% ionized in water and show no difference in strength.

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### Equilibrium Constant

$$aA + bB + \dots \rightleftharpoons cC + dD + \dots$$

$$K = \frac{[C]^c [D]^d \dots}{[A]^a [B]^b \dots}$$

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## Standard State

1. Solution concentration ( $[X]$ ) unit: M (mol/L).
2. Gas concentrations (partial pressure): atm.
3. The concentrations of pure solids, pure liquids, and solvents are omitted because they are (constant) unity.
4.  $K = f(T)$ .
5. Only thermodynamic (tendency) rather than kinetic (reaction rate) conditions are considered.

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**TABLE 9-2**  
Equilibria and Equilibrium Constants Important in Analytical Chemistry

Type of Equilibrium	Name and Symbol of Equilibrium-Constant	Typical Example	Equilibrium-Constant Expression
Dissociation of water	Ion-product constant, $K_w$	$2\text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{OH}^-$	$K_w = [\text{H}_3\text{O}^+][\text{OH}^-]$
Heterogeneous equilibrium between a slightly soluble substance and its ions in a saturated solution	Solubility product, $K_{sp}$	$\text{BaSO}_4(s) \rightleftharpoons \text{Ba}^{2+} + \text{SO}_4^{2-}$	$K_{sp} = [\text{Ba}^{2+}][\text{SO}_4^{2-}]$
Dissociation of a weak acid or base	Dissociation constant, $K_a$ or $K_b$	$\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightleftharpoons \text{H}_3\text{O}^+ + \text{CH}_3\text{COO}^-$ $\text{CH}_3\text{COO}^- + \text{H}_2\text{O} \rightleftharpoons \text{OH}^- + \text{CH}_3\text{COOH}$	$K_a = \frac{[\text{H}_3\text{O}^+][\text{CH}_3\text{COO}^-]}{[\text{CH}_3\text{COOH}]}$ $K_b = \frac{[\text{OH}^-][\text{CH}_3\text{COOH}]}{[\text{CH}_3\text{COO}^-]}$
Formation of a complex ion	Formation constant, $\beta_n$	$\text{Ni}^{2+} + 4\text{CN}^- \rightleftharpoons \text{Ni}(\text{CN})_4^{2-}$	$\beta_4 = \frac{[\text{Ni}(\text{CN})_4^{2-}]}{[\text{Ni}^{2+}][\text{CN}^-]^4}$
Oxidation/reduction equilibrium	$K_{\text{redox}}$	$\text{MnO}_4^- + 5\text{Fe}^{2+} + 8\text{H}^+ \rightleftharpoons \text{Mn}^{2+} + 5\text{Fe}^{3+} + 4\text{H}_2\text{O}$	$K_{\text{redox}} = \frac{[\text{Mn}^{2+}][\text{Fe}^{3+}]^5}{[\text{MnO}_4^-][\text{Fe}^{2+}]^5[\text{H}^+]^8}$
Distribution equilibrium for a solute between immiscible solvents	$K_d$	$I_2(\text{aq}) \rightleftharpoons I_2(\text{org})$	$K_d = \frac{[I_2]_{\text{org}}}{[I_2]_{\text{aq}}}$

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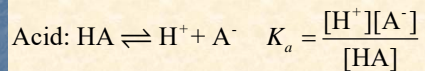
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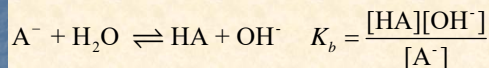
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## Calculation of $K_a$ or $K_b$ from its Conjugate $K_b$ or $K_a$



Conjugate base of HA acid,  $\text{A}^-$



$$K_a \cdot K_b = \frac{[\text{H}^+][\text{A}^-]}{[\text{HA}]} \cdot \frac{[\text{HA}][\text{OH}^-]}{[\text{A}^-]} = [\text{H}^+][\text{OH}^-] = K_w$$

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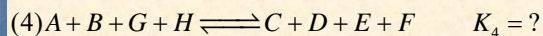
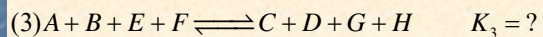
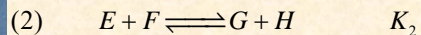
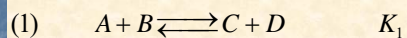
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### Manipulating Equilibrium Constants



[Class practice]

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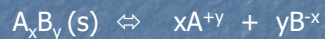
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### Solubility Product Constant ( $K_{sp}$ )

In General: (For sparingly soluble compounds)



$$K = \frac{[A^{+y}]^x [B^{-x}]^y}{[A_x B_y]}$$

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

{ $[A_x B_y]$  (solid) is constant}

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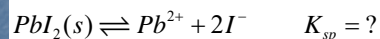
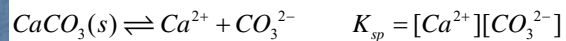
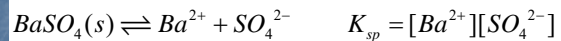
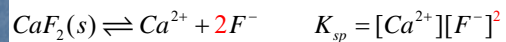
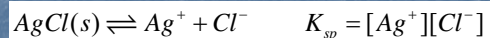
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### Examples of $K_{sp}$ Expression



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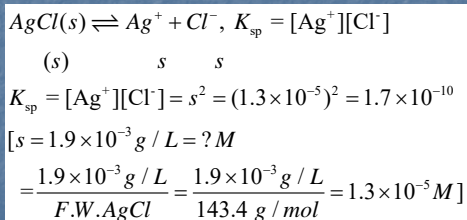
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### Calculating $K_{sp}$ from the Solubility

- If the solubility of AgCl is  $1.9 \times 10^{-3}$  g/L, what would be the  $K_{sp}$ ?



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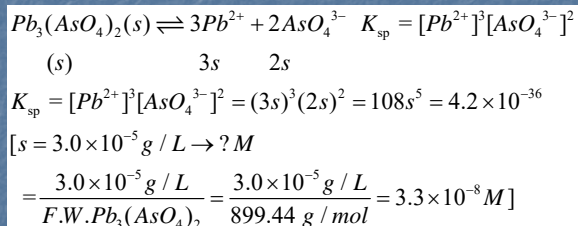
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- The solubility of lead(II) arsenate,  $Pb_3(AsO_4)_2$ , is  $3.0 \times 10^{-5}$  g/L, calculate its  $K_{sp}$ .



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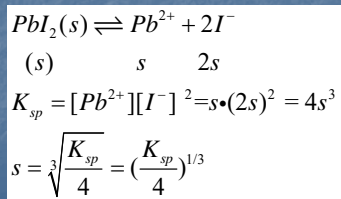
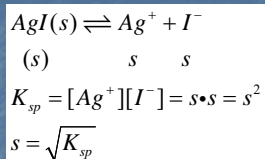
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### Calculating Solubility from $K_{sp}$



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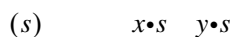
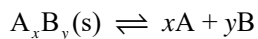
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A general expression for a precipitate dissociation



$$K_{sp} = [A]^x [B]^y = [x \cdot s]^x [y \cdot s]^y = x^x \cdot y^y \cdot s^{(x+y)}$$

$$s^{(x+y)} = \frac{K_{sp}}{x^x \cdot y^y}; \quad s = \left( \frac{K_{sp}}{x^x \cdot y^y} \right)^{\frac{1}{x+y}}$$

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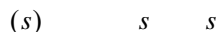
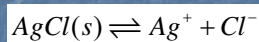
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### Solubility of a Precipitate in Pure Water

- How many grams of AgCl (fw = 143.32) can be dissolved in 100.00 mL of water at 25 °C? ( $K_{sp} [\text{AgCl}] = 1.82 \times 10^{-10}$ )



$$K_{sp} = [\text{Ag}^+][\text{Cl}^-] = s \cdot s = s^2$$

$$s = (K_{sp})^{1/2} = (1.82 \times 10^{-10})^{1/2}$$

$$= \sqrt{1.82} \times 10^{-5} = 1.35 \times 10^{-5} M$$

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- How many grams of AgCl (fw = 143.32) can be dissolved in 100.00 mL of water at 25 °C? [from previous calculation:  $s = 1.35 \times 10^{-5} M$ ]

$$\text{weight} = (\# \text{ of moles}) \times \text{formula weight}$$

$$= (C \cdot V) \times \text{formula weight} \quad (C = s)$$

$$= [1.35 \times 10^{-5} (M) \cdot 100.00 \times 10^{-3} (L)] \times 143.32 (g / mol)$$

$$= 2.0 \times 10^{-4} g = 0.20 \text{ mg}$$

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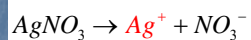
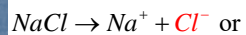
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## The Common Ion Effect

In  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$  system, add a strong electrolyte containing  $\text{Ag}^+$  or  $\text{Cl}^-$  ions (the same as the dissociated ions—common ions)

*e.g.,*

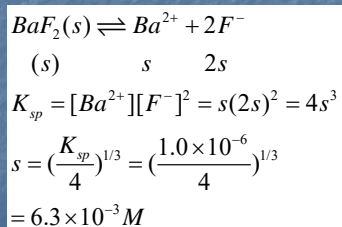


- In the presence of common ions, the solubility of the precipitate will dramatically decrease—**Common Ion Effect**. [Le Chatelier's Law]

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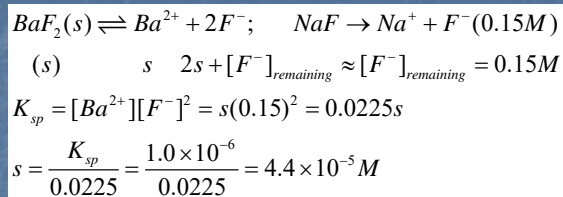
□ Calculate the solubility of slightly soluble barium fluoride,  $\text{BaF}_2$ , in (a) pure water, and (b) 0.15 M NaF. ( $K_{sp} = 1.0 \times 10^{-6}$ )

(a) In pure water



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(b) In 0.15 M NaF



Check the assumption:

$$2s + [\text{F}^-] = 8.8 \times 10^{-5} + 0.15 = 0.15 M$$

Assumption was valid.

$\text{BaF}_2$  solubility in 0.15 M NaF is ~1/140 times that in pure water.

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- **Class Practice:** Calculate the molar solubility of  $\text{Ag}_2\text{CO}_3$  in a solution that is 0.0200 M in  $\text{Na}_2\text{CO}_3$ . ( $K_{sp} = 8.1 \times 10^{-12}$ )

(key:  $1.0 \times 10^{-5}$  M)

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- **EXAMPLE:** Calculate the molar solubility of  $\text{Ag}_2\text{CO}_3$  that results when 200. mL of 0.0100 M  $\text{AgNO}_3$  is mixed with 100. mL of 0.100 M  $\text{Na}_2\text{CO}_3$ .  $K_{sp} = 8.1 \times 10^{-12}$

*The chemical reaction :*

$$2\text{AgNO}_3 + \text{Na}_2\text{CO}_3 \rightleftharpoons \text{Ag}_2\text{CO}_3(s) + 2\text{NaNO}_3$$

moles	2	1	→	1	2
initial moles	$\frac{0.0100 \times 200.}{1000}$	$\frac{0.100 \times 100.}{1000}$		0	0
	0.002	0.01		(2:10 molar ratio, $\text{Na}_2\text{CO}_3$ in excess)	
At eq. moles	0	$0.01 - \frac{1}{2}(0.002)$		$\frac{1}{2}(0.002)$	0.002
		0.009		0.001	0.002

$[\text{CO}_3^{2-}] = \frac{\text{\# of moles}}{\text{solution volume in L}} = \frac{0.009}{0.200 + 0.100} = 0.030 \text{ M}$

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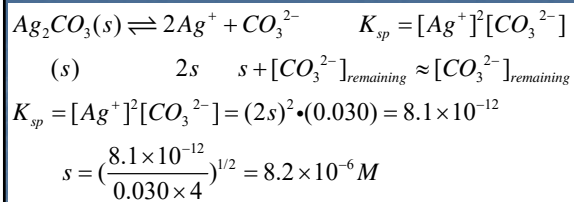
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*Check the assumption :*

$$[\text{CO}_3^{2-}] = s + [\text{CO}_3^{2-}]_{\text{remaining}} = 8.2 \times 10^{-6} + 0.030 \approx 0.030 \text{ M}$$

*Assumption was valid!*

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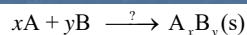
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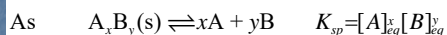
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## Precipitation Calculations



initial conc.  $[\text{A}]_i$   $[\text{B}]_i$  0



Solubility quotient ( $Q_c$ ) (or ion product)

$$Q_c = [\text{A}]_i^x [\text{B}]_i^y$$

If  $Q_c > K_{sp}$ , precipitation occurs (saturated solution)

If  $Q_c < K_{sp}$ , NO precipitation (unsaturated solution)

If  $Q_c = K_{sp}$ , the reaction mixture is at equilibrium

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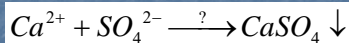
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□ Suppose a solution has  $[\text{Ca}^{2+}]$  and  $[\text{SO}_4^{2-}]$  of 0.0052 M and 0.0041 M, respectively. If these concentrations were doubled by evaporating half the water in the solution, would precipitation of  $\text{CaSO}_4$  occur given that the  $K_{sp}$  for calcium sulfate is  $2.4 \times 10^{-5}$ ?

**Solution:**



$$Q_c = [\text{Ca}^{2+}][\text{SO}_4^{2-}] = (0.0052 \times 2)(0.0041 \times 2) \\ = 8.83 \times 10^{-5} \gg K_{sp}$$

You would expect precipitation to occur.

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□ A solution of 0.00016 M lead(II)nitrate,  $\text{Pb}(\text{NO}_3)_2$ , was poured into 456 mL of 0.00023 M sodium sulfate,  $\text{Na}_2\text{SO}_4$ . Would a precipitate of lead(II)sulfate,  $\text{PbSO}_4$ , be expected to form if 255 mL of the lead nitrate solution were added? (The  $K_{sp}$  for lead(II)sulfate is  $1.7 \times 10^{-8}$ )

**Solution:**



$$Q_c = [\text{Pb}^{2+}][\text{SO}_4^{2-}] = \frac{(C \cdot V)_{\text{Pb}^{2+}}}{V_{\text{total}}} \cdot \frac{(C \cdot V)_{\text{SO}_4^{2-}}}{V_{\text{total}}} \\ = \frac{(0.00016\text{M} \cdot 255\text{mL})}{(456 + 255)\text{mL}} \cdot \frac{(0.00023 \cdot 465)}{(456 + 255)\text{mL}} \\ = 5.74 \times 10^{-5}\text{M} \cdot 1.48 \times 10^{-4}\text{M} \\ = 8.48 \times 10^{-9} < K_{sp}$$

You would NOT expect precipitation to occur.

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### Completeness of Precipitation

□ Lead chromate,  $\text{PbCrO}_4$ , is a yellow pigment used in paints. Suppose 0.50 L of a  $1.0 \times 10^{-5}$  M  $\text{Pb}(\text{C}_2\text{H}_3\text{O}_2)_2$  and 0.50 L of a  $1.0 \times 10^{-3}$  M  $\text{K}_2\text{CrO}_4$  solution are mixed. Calculate the equilibrium concentration of  $\text{Pb}^{2+}$  ion remaining in the solution after  $\text{PbCrO}_4$  precipitates. What is the percentage of  $\text{Pb}^{2+}$  remaining in solution after the precipitation has occurred. (The  $K_{sp}$  for  $\text{PbCrO}_4$  is  $1.8 \times 10^{-14}$ ).

	$\text{Pb}^{2+}$	$\text{CrO}_4^{2-}$	$\rightleftharpoons$	$\text{PbCrO}_4(\text{s})$
Ini. # moles	$0.50 \times 1.0 \times 10^{-5}$	$0.50 \times 1.0 \times 10^{-3}$		0
	$= 5.0 \times 10^{-6}$	$= 5.0 \times 10^{-4}$		0
Final. # moles	0	$5.0 \times 10^{-4} - 5.0 \times 10^{-6}$		$5.0 \times 10^{-6}$
Final. Conc. (M)	0	$4.95 \times 10^{-4}$		$5.0 \times 10^{-6}$

*i.e.*, solid  $\text{PbCrO}_4$  is in contact with a solution containing  $4.95 \times 10^{-4}$  M  $\text{CrO}_4^{2-}$  ions.

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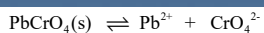
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[Initial]		0	$4.95 \times 10^{-4}$
[At e.q.]	(s)	s	$4.95 \times 10^{-4} + s \approx 4.95 \times 10^{-4}$

$$K_{sp} = [\text{Pb}^{2+}][\text{CrO}_4^{2-}] = s \cdot (4.95 \times 10^{-4}) = 1.8 \times 10^{-14}$$

$$s = [\text{Pb}^{2+}] = 3.6 \times 10^{-11} \text{ M}$$

$$\% \text{ of } \text{Pb}^{2+} \text{ in solution vs precipitated: } \frac{3.6 \times 10^{-11}}{5.0 \times 10^{-6}} \times 100\% = 7.3 \times 10^{-4}\%$$

**A complete precipitation!**

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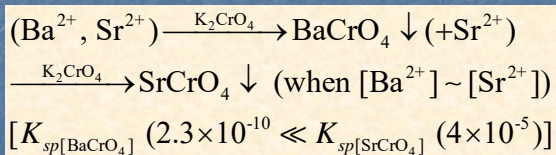
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### Fractional Precipitation

Fractional precipitation is the technique of separating two or more ions from a solution by adding a reactant that precipitates first one ion, then another, and so forth.



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## Separation by Precipitation

**EXAMPLE:** Can  $\text{Fe}^{3+}$  and  $\text{Mg}^{2+}$  be separated quantitatively as hydroxides from a solution that is 0.10 M in each cation? If the separation is possible, what range of  $\text{OH}^-$  concentrations is permissible.

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}$$

$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 7.1 \times 10^{-12}$$

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Assume quantitative separation requires that the concentration of the less soluble material to have decreased to  $< 1 \times 10^{-6}$  M before the more soluble material begins to precipitate.

Assume  $[\text{Fe}^{3+}] = 1.0 \times 10^{-6}$  M

What will be the  $[\text{OH}^-]$  required to reduce the  $[\text{Fe}^{3+}]$  to  $[\text{Fe}^{3+}] = 1.0 \times 10^{-6}$  M ?

$$K_{\text{sp}} = [\text{Fe}^{3+}][\text{OH}^-]^3 = 2 \times 10^{-39}$$

$$[\text{OH}^-]^3 = \frac{2 \times 10^{-39}}{1.0 \times 10^{-6}} = 2 \times 10^{-33}$$

$$[\text{OH}^-] = 1.3 \times 10^{-11} \text{ M}$$

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$$K_{\text{sp}} = [\text{Mg}^{2+}][\text{OH}^-]^2 = 7.1 \times 10^{-12}$$

What  $[\text{OH}^-]$  is required to begin the precipitation of  $\text{Mg}(\text{OH})_2$ ?

$$[\text{Mg}^{+2}] = 0.10 \text{ M}$$

$$(0.10 \text{ M})[\text{OH}^-]^2 = 7.1 \times 10^{-12}$$

$$[\text{OH}^-]^2 = \frac{7.1 \times 10^{-12}}{0.10} = 7.1 \times 10^{-11}$$

$$[\text{OH}^-] = 8.4 \times 10^{-6} \text{ M}$$

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Since  $1.3 \times 10^{-11}$  M is less than  $8.4 \times 10^{-6}$  M, the  $\text{Fe}^{3+}$  will be quantitatively removed long before the  $\text{Mg}(\text{OH})_2$  begins to form. Therefore, the separation is possible between  $[\text{OH}^-] 1.3 \times 10^{-11}$  M and  $[\text{OH}^-] = 8.4 \times 10^{-6}$  M. (pH range?)

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Which compound has the *lowest* molar solubility in water?

- (A)  $\text{AgBr}$  ( $K_{sp} = 5.0 \times 10^{-13}$ )  
 (B)  $\text{PbI}_2$  ( $K_{sp} = 7.9 \times 10^{-9}$ )  
 (C)  $\text{HgI}_2$  ( $K_{sp} = 1.3 \times 10^{-19}$ )  
 (D)  $\text{AgI}$  ( $K_{sp} = 8.3 \times 10^{-17}$ )

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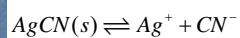
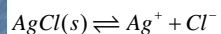
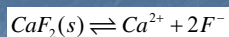
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### Effect of pH on Solubility

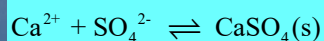


What changes in their solubilities if

(1) + HCl

(2) +  $\text{HNO}_3$

(3) +  $\text{H}_2\text{SO}_4$



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Which of the following does affect the solubility of a precipitate ?

- (A) the number of grams of the salt placed in the solution
- (B) the temperature of the solution
- (C) the ionic strength of the solution
- (D) the presence in the solution of an ion common to the insoluble salt

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In which solution is the low solubility salt  $\text{CaF}_2$  most soluble?

- (A) 0.010 M  $\text{HNO}_3$
- (B) 0.010 M  $\text{KNO}_3$
- (C) 0.010 M  $\text{Ca}(\text{NO}_3)_2$
- (D) 0.010 M  $\text{NaF}$

A saturated solution of  $\text{Cu}(\text{II})$  hydroxide has a pH of 10. Calculate the  $K_{\text{sp}}$  for the  $\text{Cu}(\text{II})$  hydroxide.

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## Acid-Base Dissociation Constants

### Example

Calculating concentrations of  $\text{H}_3\text{O}^+$  and  $\text{OH}^-$  in solutions of a strong acid or base.

Calculate the concentrations of hydronium ion and hydroxide ion at  $25^\circ\text{C}$  in 0.10 M  $\text{HCl}$ .

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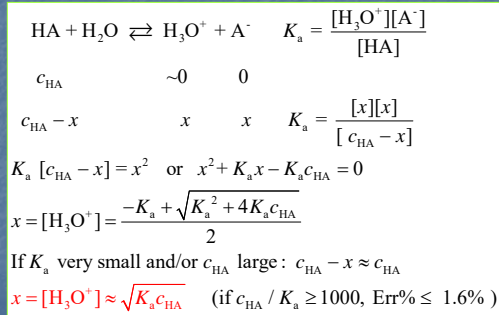
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## [H<sub>3</sub>O<sup>+</sup>] Calculation of Weak Acids



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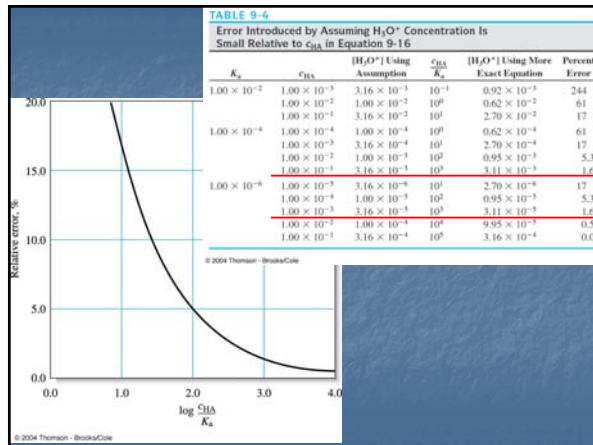
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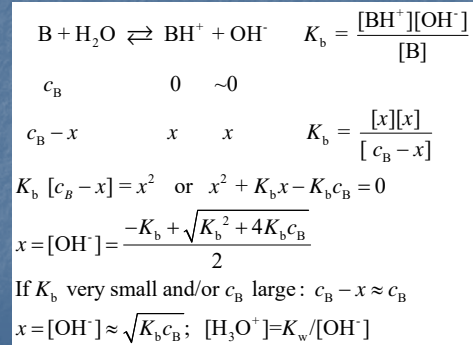
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## [OH<sup>-</sup>] Calculation of Weak Bases



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## Buffer Solutions

A **buffer** is a solution characterized by the ability to **resist changes in pH** with dilution or with addition of limited amounts of acid or base.

Buffers contain either a **weak acid and its conjugate base** or a **weak base and its conjugate acid**.

Thus, a buffer solution contains both an acid species and a base species in **equilibrium**.

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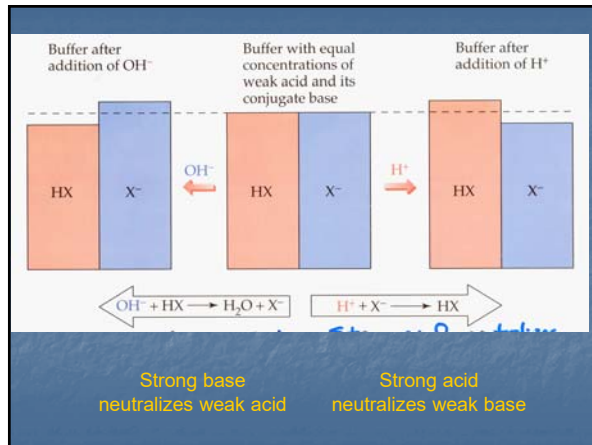
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How do we calculate the pH of a buffer ?

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Consider mixture of salt NaA and weak acid HA.

$$\text{NaA (s)} \rightleftharpoons \text{Na}^+ \text{ (aq)} + \text{A}^- \text{ (aq)}$$

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

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

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

Take log

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

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

Henderson-Hasselbalch equation

Remember  $\text{p}X = -\log X$   
so  $\text{p}K_a = -\log K_a$

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

Assumption: Changes in  $[\text{A}^-]$  &  $[\text{HA}]$  will be negligible (within 5%) if  $\frac{K_a}{[\text{base}]} < 0.01$  &  $\frac{K_a}{[\text{acid}]} < 0.01$   
use initial conc. of acid and base to calculate pH

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### "Ladder Diagram"

more basic

$[\text{CH}_3\text{COO}^-] > [\text{CH}_3\text{COOH}]$

$\text{pH} = \text{p}K_a = 4.76 \rightarrow [\text{CH}_3\text{COO}^-] = [\text{CH}_3\text{COOH}]$

$[\text{CH}_3\text{COOH}] > [\text{CH}_3\text{COO}^-]$

more acidic

pH

$\text{CO}_3^{2-}$

$\text{p}K_{a2} = 10.329$

$\text{HCO}_3^-$

$\text{p}K_{a1} = 6.352$

$\text{H}_2\text{CO}_3$

Acid–base ladder diagram for (a) acetic acid showing the relative concentrations of  $\text{CH}_3\text{COOH}$  and  $\text{CH}_3\text{COO}^-$  and (b) Carbonic acid.

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What is the pH of a solution containing 0.30 M HCOOH and 0.52 M HCOOK? (Potassium formate)

Mixture of weak acid and conjugate base!

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

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

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

$$0.30 - x \approx 0.30$$

$$0.52 + x \approx 0.52$$

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

HCOOH  $\text{p}K_a = 3.77$

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Which of the following are buffer systems? (a) KF/HF  
(b) KBr/HBr, (c) Na<sub>2</sub>CO<sub>3</sub>/NaHCO<sub>3</sub>, (d) NaHCO<sub>3</sub>

- (a) HF is a weak acid and F<sup>-</sup> is its conjugate base  
buffer solution
- (b) HBr is a strong acid  
not a buffer solution
- (c) CO<sub>3</sub><sup>2-</sup> is a weak base and HCO<sub>3</sub><sup>-</sup> is its conjugate acid  
buffer solution
- (d) ? **Amphiprotic species**

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Calculate the pH of the 0.30 M NH<sub>3</sub>/0.36 M NH<sub>4</sub>Cl 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?

$$\text{NH}_4^+ (aq) \rightleftharpoons \text{H}^+ (aq) + \text{NH}_3 (aq)$$

$$\text{pH} = \text{p}K_a + \log \frac{[\text{NH}_3]}{[\text{NH}_4^+]}$$

$$K_a = 5.6 \times 10^{-10} \quad \text{p}K_a = 9.25$$

$$\text{pH} = 9.25 + \log \frac{[0.30]}{[0.36]} = 9.17$$

$$\rightarrow \text{pOH} = 14 - \text{pH} = 4.73 \quad [\text{OH}^-] = 1.8 \times 10^{-5} \text{ M}$$

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Calculate moles of all components. Remember we have 80.0 mL of the buffer solution @ 0.30 M NH<sub>3</sub>/0.36 M NH<sub>4</sub>Cl and 20.0 mL of 0.050 M NaOH.

Moles NH<sub>4</sub><sup>+</sup> = (0.080 L)(0.36 M) = 0.029 moles  
 Moles NH<sub>3</sub> = (0.080 L)(0.30 M) = 0.024 moles  
 Moles NaOH = (0.020 L)(0.050 M) = 0.0010 moles  
 final volume = 80.0 mL + 20.0 mL = 100 mL

start (moles)	0.029	0.0010	0.024
	$\text{NH}_4^+ (aq) + \text{OH}^- (aq) \rightarrow \text{H}_2\text{O} (l) + \text{NH}_3 (aq)$		
end (moles)	0.028	0.0	0.025

Moles/Volume(L)

$$[\text{NH}_4^+] = \frac{0.028}{0.10} \quad [\text{NH}_3] = \frac{0.025}{0.10} \quad \text{pH} = 9.25 + \log \frac{[0.25]}{[0.28]} = 9.20$$

**ΔpH = 0.03**

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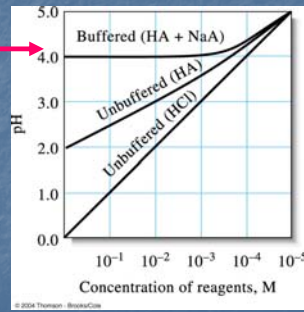
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## Property of Buffer Solutions

- The pH remains essentially independent of dilution.
- Very small changes in pH when limited amounts of acid or base are added ( $\Delta\text{pH} < 0.01$ )



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### How do we build a better buffer?

Add approximately equal quantities of acid and base  
 Have relatively high concentrations of acid and base  
 → the larger the [acid] & [base] the greater the buffer capacity

### How do we prepare a buffer at a given pH?

Choose acid/base conjugate pair from table  
 Check to be sure that they are unreactive in the system used  
 $\text{p}K_a \approx \text{pH}$  typical rule of thumb  
 $\text{pH} \pm 1 = \text{p}K_a$

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Create buffer with pH = 7.50.

$$\text{pH} \pm 1 = \text{p}K_a$$

Look for  $\text{p}K_a$ 's 6.5 → 8.5

$$\Rightarrow K_a\text{'s } 3 \times 10^{-7} \rightarrow 3 \times 10^{-9}$$

OK?

$\text{HOCl} / \text{OCl}^-$	$K_a = 3.5 \times 10^{-8}$
$\text{H}_2\text{PO}_4^- / \text{HPO}_4^{2-}$	$K_{a2} = 6.2 \times 10^{-8}$
$\text{H}_2\text{AsO}_4^- / \text{HAsO}_4^{2-}$	$K_{a2} = 8 \times 10^{-8}$
$\text{H}_2\text{CO}_3 / \text{HCO}_3^-$	$K_{a1} = 4.3 \times 10^{-7}$

Calculate quantities of acid and base.

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

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$$\text{H}_2\text{CO}_3 / \text{HCO}_3^- \quad K_{a1} = 4.3 \times 10^{-7}$$

$$pK_{a1} = 6.37$$

$$\text{pH} - pK_a = \log \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$

$$7.50 - 6.37 = 1.13$$

$$10^{-1.13} = 13.6 = \frac{[\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]}$$
 Set  $[\text{H}_2\text{CO}_3] = 0.0100 \text{ M}$  (NOTE: This is a judgment call.)  
 then  $[\text{HCO}_3^-] = 13.6 [\text{H}_2\text{CO}_3] = 0.136 \text{ M}$

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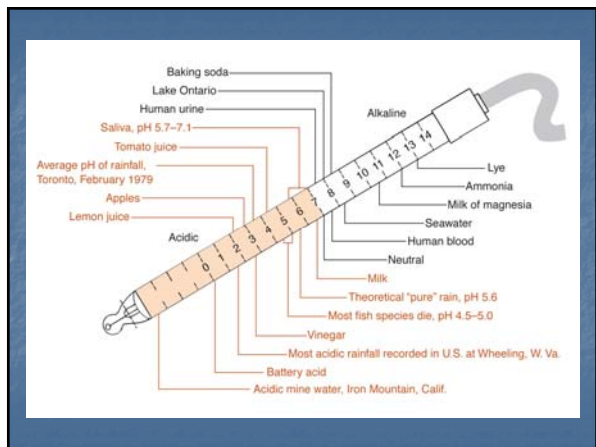
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### Chapter 9 Summary

- Classification of electrolytes
- Common-ion effect
- Equilibrium constants
- Acids and bases
- Ion-product of water
- Acid-base dissociation
- Conjugate acid-base pairs
- Buffer capacity
- Buffer solutions
- Amphiprotic species
- Autoprotolysis
- Solubility product

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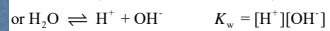
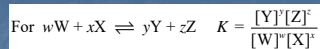
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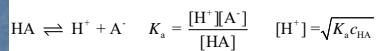
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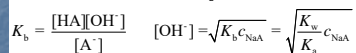
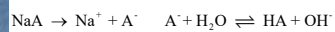
## Important Equations



Weak acid HA



Weak base NaA



Buffer solution--Henderson-Hasselbalch equation

weak acid/conj. base or weak base/conj. acid

$pH = pK_a + \log \frac{[Base]}{[Acid]} = pK_a + \log \frac{c_{NaA}}{c_{HA}}$

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