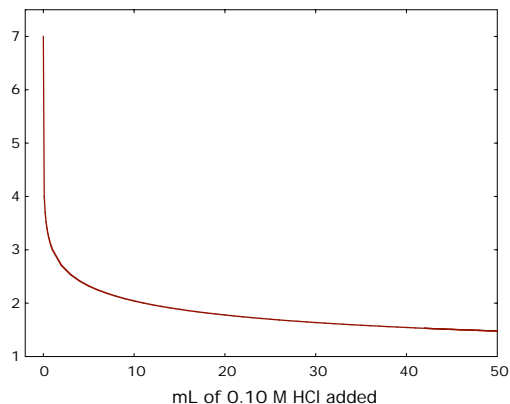


Buffer Solutions

pH of solution adding 0.10 M HCl to 100 mL water

HCl added	pH
0 mL	7.00
2 mL	2.71
5 mL	2.32
10 mL	2.04
20 mL	1.78
50 mL	1.48



Buffer Solutions

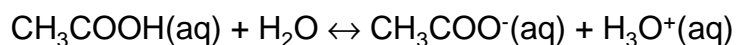
- v A buffer helps a solution maintain its pH when acid or base is added
- v A buffer must contain two components to work
 - v a weak acid that reacts with added base
 - v a weak base that reacts with added acid
- v Buffers usually contain approximately equal amounts of a weak acid and its conjugate base



Buffer Solutions

Solution that is 0.100 M CH_3COOH (acetic acid)
and 0.100 M NaCH_3COO (sodium acetate)

Find pH of buffer solution:

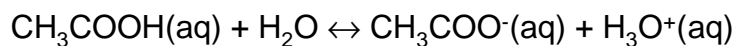


	$[\text{CH}_3\text{COOH}]$	$[\text{CH}_3\text{COO}^-]$	$[\text{H}_3\text{O}^+]$
initial	0.100	0.100	≈ 0
Δ	-x	x	x
equil	$0.100 - x$	$0.100 + x$	x



Buffer Solutions

Find pH of buffer solution:



$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(.100 + x)x}{(.100 - x)} = 1.8 \times 10^{-5}$$

assume x is negligible
compared to .100 M

$$x = 1.80 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.74$$

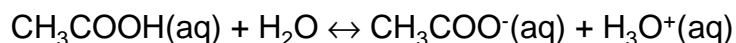


Buffer Solutions

Add 5 mL .10 M HCl

Find pH of resulting solution

Assume all acid added reacts with acetate ion to form acetic acid (remember that acids react with bases)



$$[\text{H}_3\text{O}^+] \text{ added} = (5 \text{ mL})(.10 \text{ M})/(105 \text{ mL}) = 4.76 \times 10^{-3} \text{ M}$$

$$[\text{CH}_3\text{COOH}] = 0.100 + 0.005 = 0.105 \text{ M}$$

$$[\text{CH}_3\text{COO}^-] = 0.100 - 0.005 = 0.095 \text{ M}$$



Buffer Solutions

Now let solution come to equilibrium

	$[\text{CH}_3\text{COOH}]$	$[\text{CH}_3\text{COO}^-]$	$[\text{H}_3\text{O}^+]$
initial	.105	.095	≈ 0
Δ	-x	x	x
equil	$.105 - x$	$.095 + x$	x

$$K_a = \frac{[\text{CH}_3\text{COO}^-][\text{H}_3\text{O}^+]}{[\text{CH}_3\text{COOH}]} = \frac{(.095 + x)x}{(.105 - x)} = 1.8 \times 10^{-5}$$

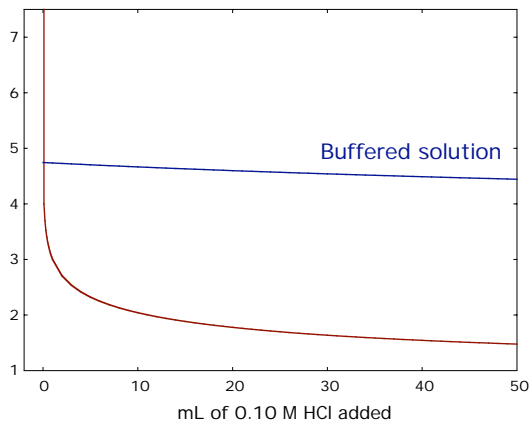
$$x = 1.99 \times 10^{-5} \text{ M}$$

$$\text{pH} = 4.71$$

Buffer Solutions

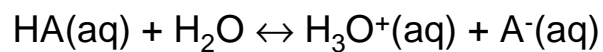
pH of buffered solution adding 0.10 M HCl to 100 mL soln

HCl added	pH
0 mL	4.74
5 mL	4.71
10 mL	4.66
15 mL	4.58
25 mL	4.57
50 mL	4.45



Buffer Solutions

- v Henderson-Hasselbach Equation
- v Allows calculation of pH of a buffer if concentrations of conjugate acid and conjugate base are known



$$K_a = \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

$$[\text{H}_3\text{O}^+] = \frac{K_a[\text{HA}]}{[\text{A}^-]}$$



Buffer Solutions

- v Take -log of both sides

$$-\log[H_3O^+] = -\log\left\{\frac{K_a[HA]}{[A^-]}\right\} = -\log(K_a) - \log\left(\frac{[HA]}{[A^-]}\right)$$

$$-\log(K_a) = pK_a \qquad -\log\left(\frac{[HA]}{[A^-]}\right) = \log\left(\frac{[A^-]}{[HA]}\right)$$

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \qquad \text{Henderson-Hasselbach Eqn}$$



Buffer Solutions

- v Using the Henderson-Hasselbach Eqn, we can:
 - v Determine pH of a solution
 - v Determine ratio of conjugate base to conjugate acid to achieve specific pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right)$$



Buffer Solutions

- v Let's go back to problem of adding HCl to buffer solution:
- v We can use H-H eqn. to make the calculations much easier

$$[\text{CH}_3\text{COOH}] = 0.100 + [\text{HCl}]_{\text{added}}$$

$$[\text{CH}_3\text{COO}^-] = 0.100 - [\text{HCl}]_{\text{added}}$$

$$\text{pH} = \text{pK}_a + \log\left(\frac{[\text{A}^-]}{[\text{HA}]}\right)$$



Buffer Solutions

V_{HCl}	[HCl]	$[\text{CH}_3\text{COOH}]$	$[\text{CH}_3\text{COO}^-]$	pH
5mL	$(.1)(5\text{mL})/105\text{mL}$ = .00476 M	$.100+.005$ =.105 M	$.100-.005$ =.095 M	4.70
10mL	$(.1)(10)/110$ = .00909 M	$.100+.009$ =.109 M	$.100-.009$ =.091 M	4.66
25mL	$(.1)(25)/125$ = .0200 M	$.100+.020$ =.120 M	$.100-.020$ =.080 M	4.56
50mL	$(.1)(50)/150$ = .0333 M	$.100+.033$ =.133 M	$.100-.033$ =.067 M	4.44



Buffer Solutions

- v Buffer Capacity—the amount of acid or base that can be added to a buffer without the pH significantly changing
- v Suppose we add acid to a buffer solution:
 - v The acid will react with the conjugate base until it is depleted
 - v Past this point, the solution behaves as if no buffer were present



Acid-Base Titrations

- v A titration is a method used to determine the concentration of an unknown species
- v Add a measured amount of a known reactant
- v Determine when the reaction has gone to completion

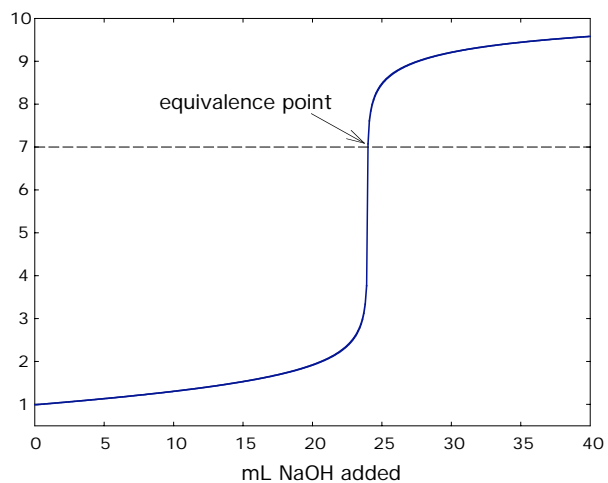


- v At the equivalence point
moles unknown = moles known added

$$C_{\text{unknown}} V_{\text{unknown}} = C_{\text{known}} V_{\text{known}}$$

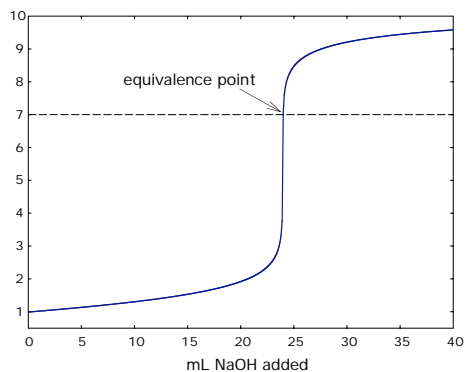
Acid-Base Titrations

Titrate 50.00 mL unknown HCl soln. with 0.2137 M NaOH



Acid-Base Titrations

At equivalence point, V_{NaOH}
= 23.96 mL
 $\text{mol}(\text{NaOH}) =$
 $(.2137 \text{ M})(.02396 \text{ L})$
 $= 5.120 \times 10^{-3} \text{ mol}$
 $\text{mol}(\text{HCl}) = 5.120 \times 10^{-3} \text{ mol}$
(mol known = mol unknown)
 $[\text{HCl}] =$
 $(5.120 \times 10^{-3} \text{ mol}) / (.05000 \text{ L})$
 $= 0.1024 \text{ M}$





Indicators

- v An indicator is a chemical species that changes color depending on the pH of the solution
- v An indicator is a conjugate acid-conjugate base pair in which the acid and base forms of the compound have different colors
$$\begin{array}{ccc} \text{HIn}(\text{aq}) + \text{H}_2\text{O} & \rightarrow & \text{In}^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \\ \text{color 1} & & \text{color 2} \end{array}$$
- v Indicators are used to determine the endpoint of a titration

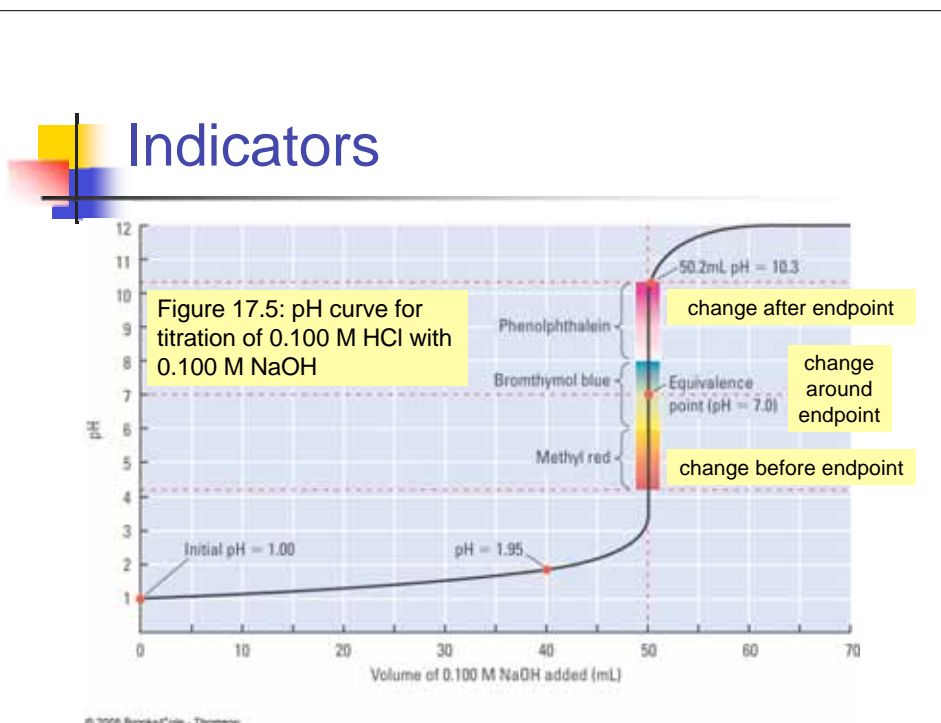


Indicators

- v The pK_a of the indicator determines the pH range over which the color changes
$$\begin{array}{ll} [\text{HIn}]/[\text{In}^-] \geq 10 & \text{acid color} \\ [\text{HIn}]/[\text{In}^-] \approx 0.1 & \text{base color} \\ [\text{HIn}]/[\text{In}^-] \approx 1 & \text{intermediate color} \end{array}$$
- v Remember: $\text{pH} = \text{pK}_a + \log\{[\text{In}^-]/[\text{HIn}]\}$
If $[\text{HIn}]/[\text{In}^-] = 1$, $\log\{[\text{HIn}]/[\text{In}^-]\} = 0$
 $\therefore \text{pH} = \text{pK}_a$ at point when indicator is changing color

Indicators

<u>Indicator</u>	<u>pK_a</u>	<u>pH range</u>	<u>color change</u>
Methyl orange	3.7	3.1 – 4.4	red to yellow
Bromophenol blue	4.0	3.0 – 4.6	yellow to blue
Methyl red	5.1	4.2 – 6.3	red to yellow
Bromothymol blue	7.0	6.0 – 7.6	yellow to blue
Phenol red	7.9	6.8 – 8.4	yellow to red
Phenolphthalein	9.3	8.2 – 10.0	clear to pink





Indicators

- v Titration of weak acid with strong base
 $\text{HA}(\text{aq}) + \text{OH}^-(\text{aq}) \rightarrow \text{A}^-(\text{aq}) + \text{H}_2\text{O}$
- v At equivalence point
 $\text{A}^-(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$
the solution is basic because conjugate base of weak acid reacts with water to form $\text{OH}^-(\text{aq})$



Indicators

- v Titrate 25.00 mL 0.100 M formic acid (HCOOH) with 0.100 M NaOH
 $K_a = 1.8 \times 10^{-4}$
- v Find pH at equivalence point and select appropriate indicator
- v At equivalence point, $\text{mol}(\text{HCOOH}) = \text{mol}(\text{OH}^-)$
 $\text{mol}(\text{fa}) = (0.100 \text{ M fa})(0.02500 \text{ L}) = 2.5 \times 10^{-3} \text{ mol}$
fa = formic acid
 $V_{\text{NaOH added}} = (2.5 \times 10^{-3} \text{ mol}) / (0.100 \text{ M}) = 25.0 \text{ mL}$
 $V_{\text{total}} = 50.0 \text{ mL}$



Indicators

- v Assume $\text{HCOOH} + \text{OH}^-$ reaction goes to completion:
 $[\text{HCOO}^-] = (2.5 \times 10^{-3} \text{ mol}) / (0.0500 \text{ L}) = 0.0500 \text{ M}$
- v Determine K_{eq} for reaction of formate ion:
 $\text{HCOO}^-(\text{aq}) + \text{H}_2\text{O} \leftrightarrow \text{HCOOH}(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_{\text{eq}} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{K_{\text{w}}}{K_{\text{a}}} = 6.67 \times 10^{-11}$$



Indicators

$$K_{\text{eq}} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{K_{\text{w}}}{K_{\text{a}}} = 6.67 \times 10^{-11}$$

	$[\text{HCOO}^-]$	$[\text{HCOOH}]$	$[\text{OH}^-]$
initial	.0500	0	0
Δ	-x	x	x
equil	.0500 - x	x	x

$$K_{\text{eq}} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{x^2}{0.0500 - x} = 6.67 \times 10^{-11}$$



Indicators

$$K_{\text{eq}} = \frac{[\text{HCOOH}][\text{OH}^-]}{[\text{HCOO}^-]} = \frac{x^2}{0.0500 - x} = 6.67 \times 10^{-11}$$

$$x = 1.83 \times 10^{-6} \text{ M} = [\text{OH}^-]$$

$$\text{pOH} = -\log(1.83 \times 10^{-6}) = 5.74$$

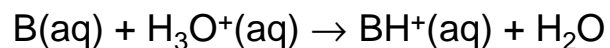
$$\text{pH} = 14.00 - 5.74 = 8.26$$

Phenol red (6.8 – 8.4) or phenolphthalein (8.2 – 10.0)
would be appropriate indicators

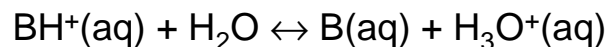


Indicators

- v Titration of weak base with strong acid

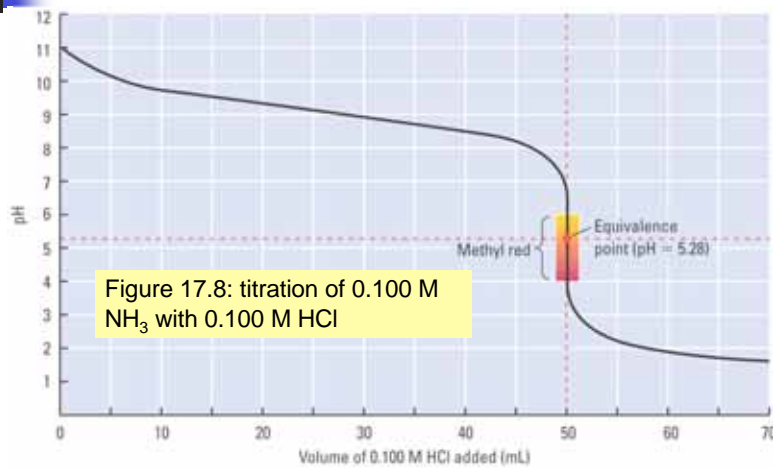


- v At equivalence point



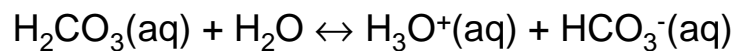
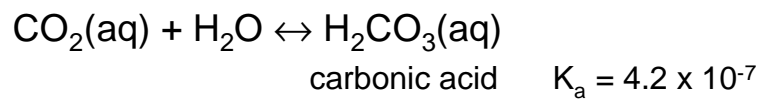
the solution is acidic because conjugate acid of
weak base reacts with water to form $\text{H}_3\text{O}^+(\text{aq})$

Indicators



Acid Rain

- Carbon dioxide in the air is in equilibrium with H_2O in atmospheric water droplets (clouds & fog):



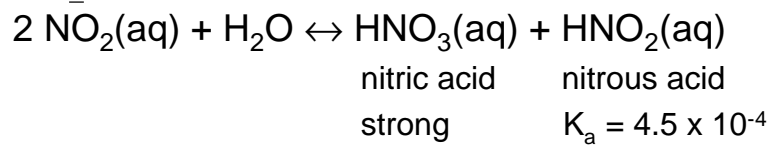
- Natural rain water has pH = 5.6



Acid Rain

- v Emitted pollutants can form additional acid sources in clouds:

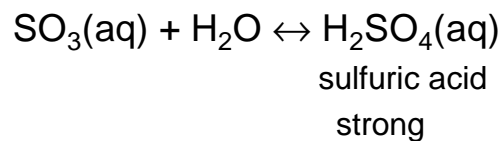
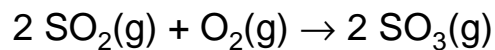
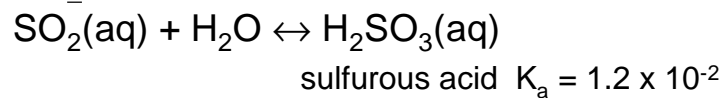
NO₂:

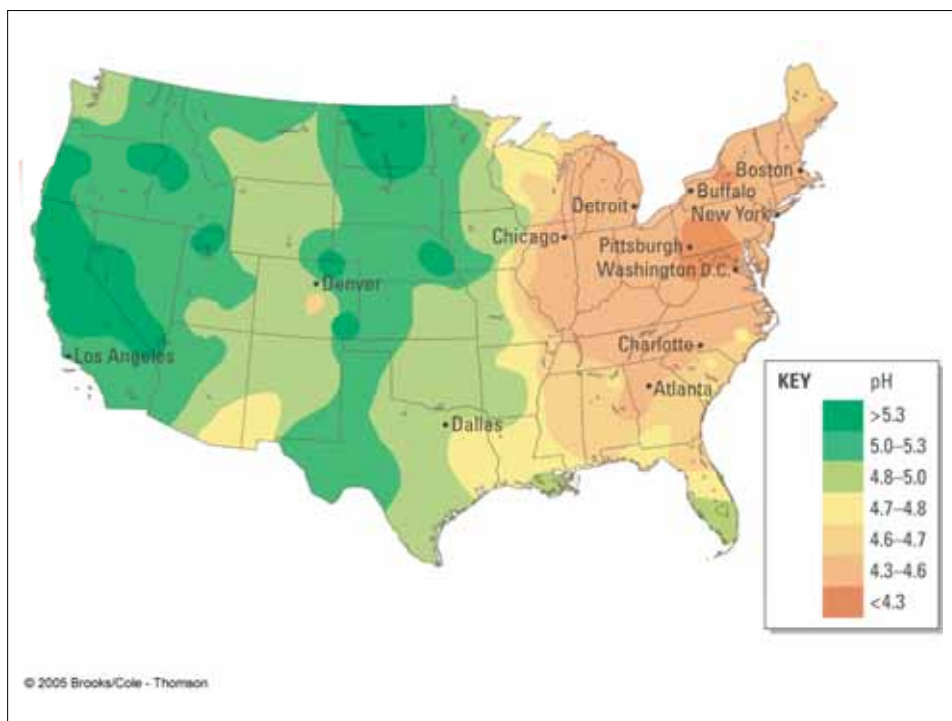


Acid Rain

- v Emitted pollutants can form additional acid sources in clouds:

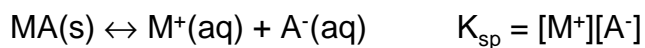
SO₂:



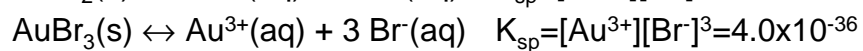
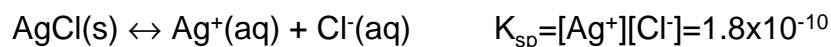


Solubility Products

- v Many salts are only slightly soluble
- v The solubility product is a measure of the concentration of ions in a solution saturated with the salt



Examples

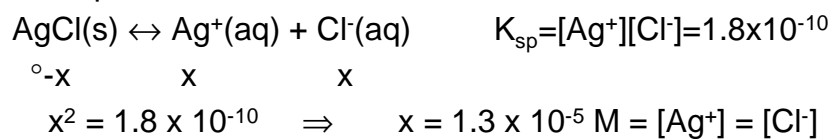




Solubility Products

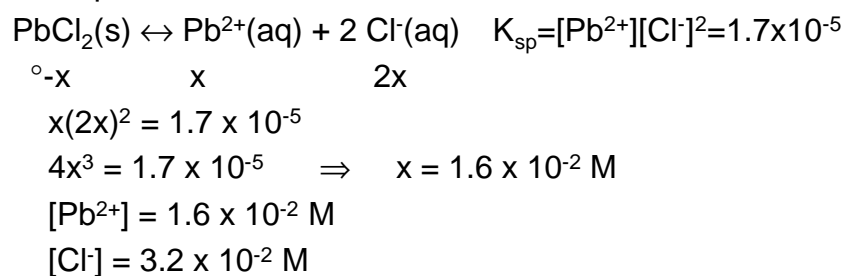
- Knowing the K_{sp} , we can calculate the concentration of ions in solution

Examples



Solubility Products

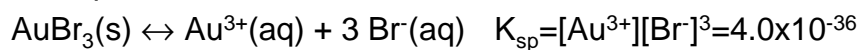
Examples





Solubility Products

Examples



$$x(3x)^3 = 4.0 \times 10^{-36}$$

$$27x^4 = 4.0 \times 10^{-36} \Rightarrow x = 6.2 \times 10^{-10} \text{ M}$$

$$[\text{Au}^{3+}] = 6.2 \times 10^{-10} \text{ M}$$

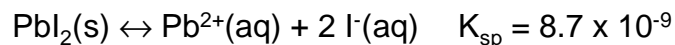
$$[\text{Br}^-] = 1.9 \times 10^{-9} \text{ M}$$



Solubility Products

Examples—Common ion effect

How much PbI_2 will dissolve in a 0.0100 M solution of NaI?



$$x(2x + .0100)^2 = 8.7 \times 10^{-9}$$

$$x(4x^2 + 0.0200x + 1.0 \times 10^{-4}) = 8.7 \times 10^{-9}$$

$$4x^3 + .0200x^2 + 1.0 \times 10^{-4}x - 8.7 \times 10^{-9} = 0$$

$$x = 8.6 \times 10^{-5} \text{ M}$$

vs $1.3 \times 10^{-3} \text{ M}$ if no $\text{I}^-(\text{aq})$ were present initially



Factors Affecting Solubility

- v Salts that are slightly soluble in water can be much more soluble in acid if one or both of its ions are moderately basic:

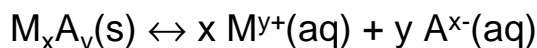


- v But $\text{CO}_3^{2-}(\text{aq})$ is the conjugate base of $\text{HCO}_3^-(\text{aq})$
 $\text{CO}_3^{2-}(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \leftrightarrow \text{HCO}_3^-(\text{aq}) + \text{H}_2\text{O} \quad K_{\text{b}} = 2.1 \times 10^{-4}$
 $\text{HCO}_3^-(\text{aq}) + \text{H}_3\text{O}^+(\text{aq}) \leftrightarrow \text{H}_2\text{CO}_3(\text{aq}) + \text{H}_2\text{O} \quad K_{\text{b}} = 2.4 \times 10^{-8}$
 $\text{H}_2\text{CO}_3(\text{aq}) \leftrightarrow \text{H}_2\text{O} + \text{CO}_2(\text{g}) \quad K_{\text{eq}} \approx 10^5$
- v Works for carbonates, some sulfides, phosphates, etc. (species that behave as bases [no too weak])



Precipitation

- v Define ion quotient, Q, as:



$$Q = [\text{M}^{y+}]^x[\text{A}^{x-}]^y$$

- v A precipitate will form only when Q exceeds K_{sp}
 - v $Q < K_{\text{sp}}$: solution is unsaturated—no precipitate
 - v $Q > K_{\text{sp}}$: solution is saturated—precipitate forms
 - v $Q = K_{\text{sp}}$: solution at saturation point