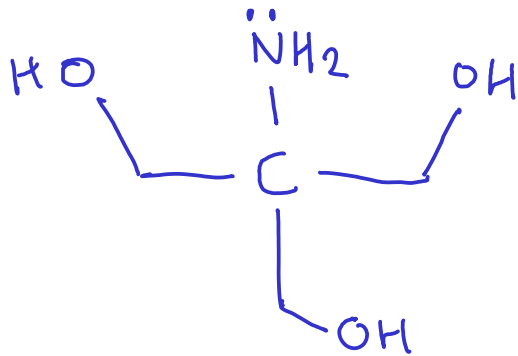
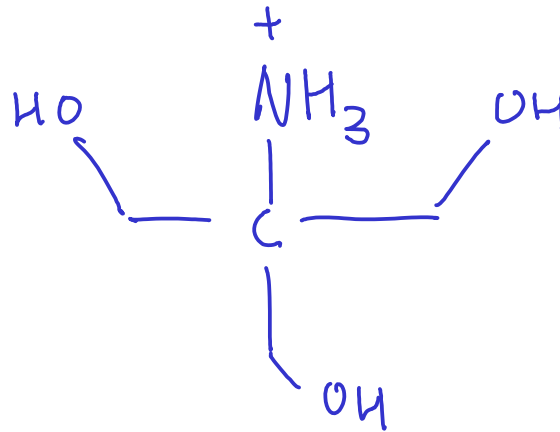


Buffer calculation: Tris buffer - Tris(hydroxymethyl)-aminomethane



tris base



tris-HCl (conjugate acid of tris base)

Cl<sup>-</sup>

$$pK_a = 8,06$$

Calculate the pH of a buffer made from 50 mL of 0.10M tris and 50 mL of 0.15M tris-HCl. Assume volumes add.

$$pH = pK_{a,acidic} + \log \left( \frac{[basic\ species]}{[acidic\ species]} \right)$$

$$[tris] : (0.10M)(50.mL) = (M_2)(100mL)$$

$$m_1v_1 = m_2v_2 \quad 0.050M tris = M_2$$

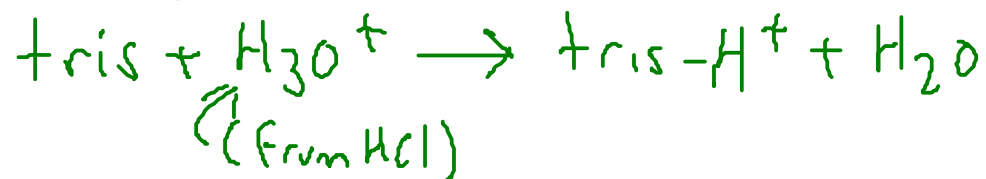
$$[tris-H^+] : (0.15M)(50.mL) = (M_2)(100mL)$$

$$0.075M tris-H^+ = M_2$$

$$pH = 8,06 + \log \left( \frac{0.050}{0.075} \right) = \boxed{7.88}$$

174 Take 100. mL of the previous buffer (0.050 M tris / 0.075 M tris-HCl), and add 5.0 mL of 0.10 M HCl. What is the pH of the mixture?

The HCl should react with basic component of the buffer (tris), and change it to its conjugate acid



... so we need to find out the NEW concentrations of each species in the system.

Species	Initial mmol	$\Delta$ in rxn	Final mmol	[conc.]
tris	100 mL $\times$ 0.050 M = 5.0 mmol	-0.5 mmol	4.5 mmol	$\frac{4.5 \text{ mmol}}{105 \text{ mL}} = 0.0428571 \text{ M}$
tris-H <sup>+</sup>	100 mL $\times$ 0.075 M = 7.5 mmol	+0.5 mmol	8.0 mmol	$\frac{8.0 \text{ mmol}}{105 \text{ mL}} = 0.0761905 \text{ M}$
HCl	5 mL $\times$ 0.10 M = 0.5 mmol	-0.5 mmol	0 mmol	0

\* Solution volume is now 105 mL (100 mL of buffer plus 5 mL of HCl)

$$\text{pH} = 8.06 + \log \left( \frac{0.0428571 \text{ M}}{0.0761905 \text{ M}} \right) = \boxed{7.81}$$

The original pH was 7.88, so the pH dropped by 0.07 pH units.

Compare this 0.07 unit pH change with adding 5.0 mL of 0.10 M HCl to 100. mL of pure water.

(We're just diluting the acid...)

$$M_1 V_1 = M_2 V_2$$

$$(0.10 \text{ M})(5.0 \text{ mL}) = M_2 (105 \text{ mL})$$

$$0.0047619 \text{ M} = M_2$$

Since this is a strong acid, hydronium ion concentration equals nominal acid concentration:

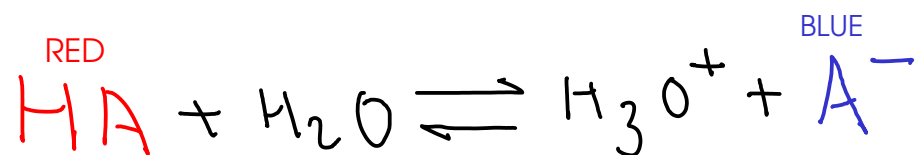
$$[\text{H}_3\text{O}^+] = 0.0047619 \text{ M}$$

$$\text{pH} = 2.32$$

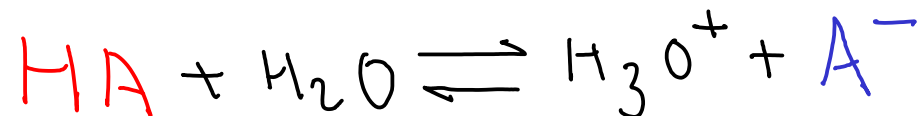
... which is a change of 4.68 pH units from water's original pH of 7.00!

## INDICATORS

- Instead of using a pH meter to monitor acidity, we may choose to use an acid-base INDICATOR.
- Acid-base indicators are weak acids or weak bases which are highly colored.
- The color of the undissociated indicator MUST BE DIFFERENT than the color of the dissociated form!



The indicator must be present in very low concentrations - so that the indicator's equilibrium DOES NOT CONTROL the pH of the solution!



Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

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

When does the color of the indicator change?

If the pH is  $\ll$  pKa, then the log term above must be both large AND negative!

- What color is the solution?



If the pH is  $\gg$  pKa, then the log term above must be both large AND positive!

- What color is the solution?



- So, the color changes when the pH of the solution is near the pKa of the indicator, BUT we can only DETECT the change when enough of the other form is present.

SOLUTION: Homogeneous mixture of substances Solutions contain:

SOLUTE: Component(s) of a solution present in small amount

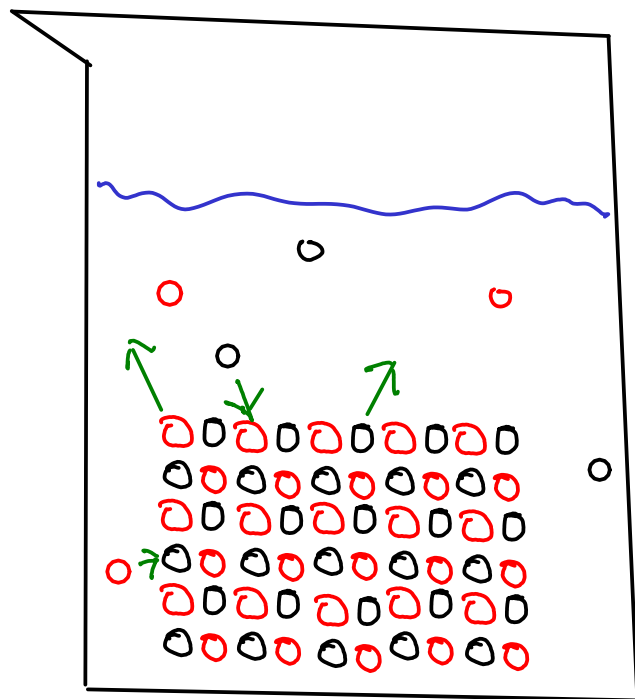
SOLVENT: Component of a solution present in greatest amount

We usually call water the solvent in aqueous mixtures, even if the water is present in smaller amount than another component

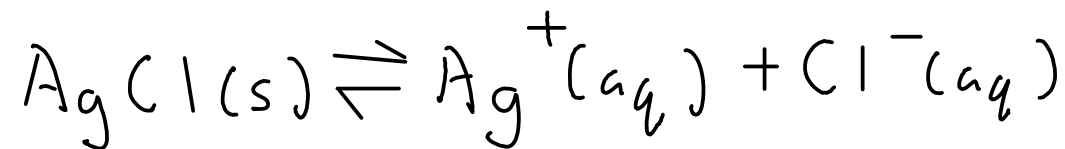
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

SATURATED SOLUTION: Contains the maximum amount of solute that it is possible to dissolve in a given volume of solvent!

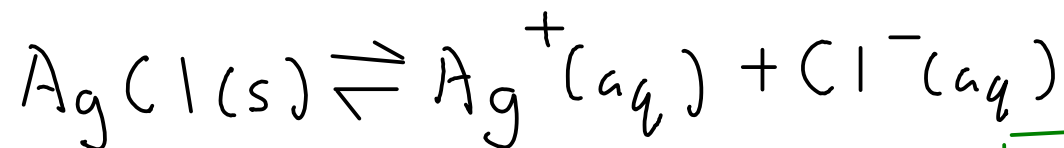
A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

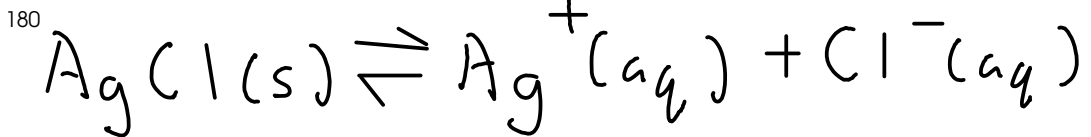


At equilibrium, the rate of dissolving equals the rate of crystallization!



$$K_c = [\text{Ag}^+][\text{Cl}^-] = 1.8 \times 10^{-10}$$

... what does this equilibrium constant tell us? That silver chloride isn't very soluble!

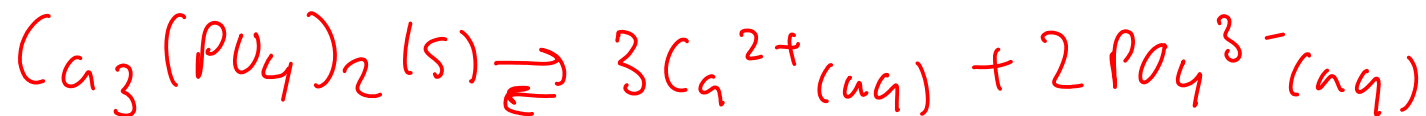


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↪ This equilibrium constant is given a special name - the SOLUBILITY PRODUCT CONSTANT - because the equilibrium expression for the dissolving of a salt always appears as a PRODUCT of the concentrations of the ions in the compound!

Remember,  $K_{sp}$  is an equilibrium constant, so everything that applies to equilibrium constants applies to the solubility constant - including what to do with coefficients:

What is the solubility product constant expression for calcium phosphate?



$$K_{sp} = [\text{Ca}^{2+}]^3 [\text{PO}_4^{3-}]^2$$

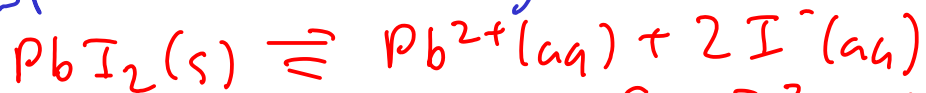


181 Solubility calculations and K<sub>sp</sub>

You can calculate the solubility of a compound if you know K<sub>sp</sub>!

Calculate the solubility (in g/L) of lead(II) iodide at 25°C. (see p A-15 in book)

$$K_{sp} = 6.5 \times 10^{-9} ; \text{FW} = 461.0 \text{ g/mol}$$



$$K_{sp} = [\text{Pb}^{2+}][\text{I}^{-}]^2 = 6.5 \times 10^{-9}$$

Species	[Initial]	Δ	[Equilibrium]
Pb <sup>2+</sup>	0	+x	x
I <sup>-</sup>	0	+2x	2x

Let "x" equal the change in Pb<sup>2+</sup> concentration...

$$(x)(2x)^2 = 6.5 \times 10^{-9}$$

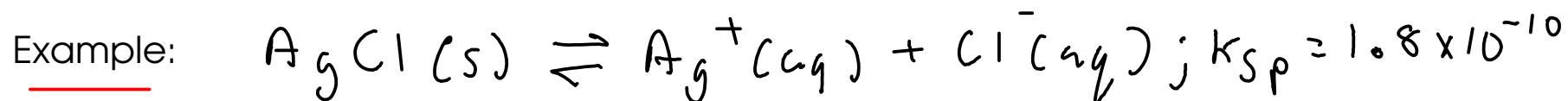
$$4x^3 = 6.5 \times 10^{-9}$$

$$x = 0.0011756673 \text{ M} = [\text{Pb}^{2+}] = [\text{PbI}_2]_{\text{dissolved}}$$

$$\frac{0.0011756673 \text{ mol PbI}_2}{\text{L}} \times \frac{461.0 \text{ g PbI}_2}{\text{mol PbI}_2} = 0.54 \text{ g PbI}_2/\text{L}$$

## <sup>182</sup> Precipitation - also known as the reaction quotient

To predict whether a salt at a given concentration will precipitate out, calculate the reaction quotient  $Q$  and compare it to the  $K_{sp}$



$$Q = [Ag^+][Cl^-]$$

IF...

- \*  $Q < K_{sp}$  ; the reaction proceeds to produce more products (dissolved ions), so more solid is able to dissolve: NO PRECIPITATION
- \*  $Q > K_{sp}$  ; the reaction proceeds to produce more reactants (solid), so solid falls out of solution: PRECIPITATION OCCURS
- \*  $Q = K_{sp}$  ; the reaction is at equilibrium. PRECIPITATION IS JUST BEGINNING

Would a solution with  $[Ag^+] = 0.014 \text{ M}$  and  $[Cl^-] = 0.00042 \text{ M}$  precipitate?

$$Q = (0.014 \text{ M})(0.00042 \text{ M}) = 5.88 \times 10^{-6}$$

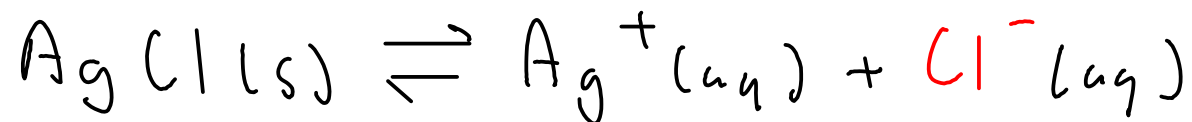
$$5.88 \times 10^{-6} > 1.8 \times 10^{-10}$$

$$Q > K_c$$

Since  $Q > K_c$ , reaction is proceeding to the LEFT which means that solid will form. PRECIPITATION OCCURS.

## <sup>183</sup> Le Chateleur's Principle

The "common ion effect" affects the solubility of a compound in solution. The presence of one of the ions in a salt in the solution will REDUCE THE SOLUBILITY of that salt!



Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

Solubility can also be affected by pH - depending on the acidic or basic properties of the salt!

A second example: Salicylic acid in the characterization lab

Calculate the solubility of AgCl (FW = 143.35 g/mol) in distilled water. Then, calculate the solubility of AgCl in 0.10 M NaCl solution. Report both answers in parts per million (mg/L)



For distilled water...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	x
$\text{Cl}^-$	0	+x	x

Let "x" equal the change in dissolved Ag<sup>+</sup> concentration.

$$(x)(x) = 1.8 \times 10^{-10}$$

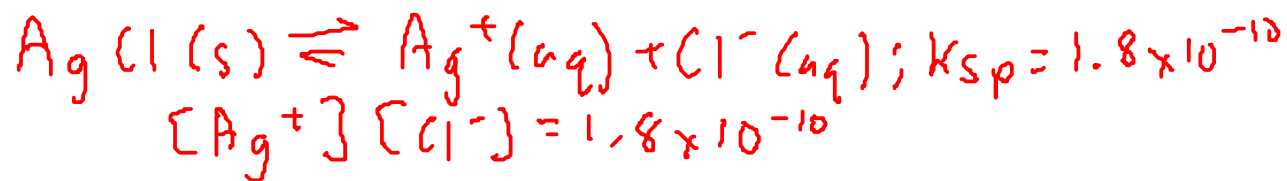
$$x^2 = 1.8 \times 10^{-10}$$

$$x = 1.341640786 \times 10^{-5} \text{ M} = [\text{Ag}^+] = [\text{AgCl}] \text{ dissolved}$$

Convert answer's units to ppm (mg/L)...

$$\frac{1.341640786 \times 10^{-5} \text{ mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} \times \frac{\text{mg}}{10^{-3} \text{ g}} = 1.9 \text{ ppm AgCl in distilled H}_2\text{O}$$

↑  
converts mol to g
↑  
converts g to mg



For solubility in 0.10 M NaCl solution...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{Ag}^+$	0	+x	x
$\text{Cl}^-$	0.10	+x	0.10 + x

$$(x)(0.10 + x) = 1.8 \times 10^{-10}$$

↓ We know that  $x \ll 0.10$ , so  $0.10 + x \approx 0.10$

$$(x)(0.10) = 1.8 \times 10^{-10}$$

$$x = 1.8 \times 10^{-9} \text{ M} = [\text{Ag}^+] = [\text{AgCl}]_{\text{dissolved}}$$

$$\frac{1.8 \times 10^{-9} \text{ mol AgCl}}{1} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} \times \frac{\text{mg}}{10^{-3} \text{ g}} = \boxed{2.6 \times 10^{-4} \text{ ppm AgCl in 0.10 M NaCl}}$$

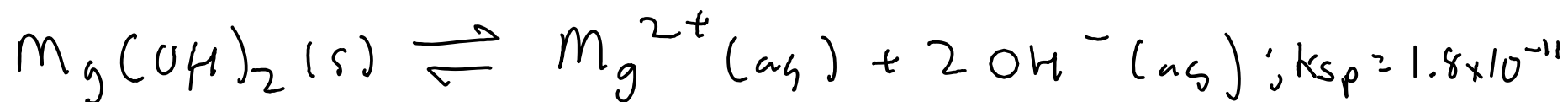
(0.00026 ppm)

Compare:

1.9 ppm AgCl in distilled water vs  
0.00026 ppm AgCl in 0.10 M NaCl

Conclusion: The presence of a common ion greatly decreases solubility

## pH AND SOLUBILITY



This compound's solubility is pH dependent. How?

\* In a BASIC solution, the concentration of hydroxide ion in solution is high, so solubility is LOWER than in pure water.

\* In an ACIDIC solution, we have a significant amount of hydronium, which can react with hydroxide. This lowers the hydroxide concentration and makes magnesium hydroxide MORE SOLUBLE

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### Generalizing

If a compound is BASIC, then it will be LESS SOLUBLE in basic solutions, and MORE SOLUBLE in acidic solutions!

If a compound is ACIDIC, then it will be MORE SOLUBLE in basic solutions, and LESS SOLUBLE in acidic solutions!

If a compound is NEUTRAL (neither acidic nor basic), then its solubility will be UNAFFECTED by pH