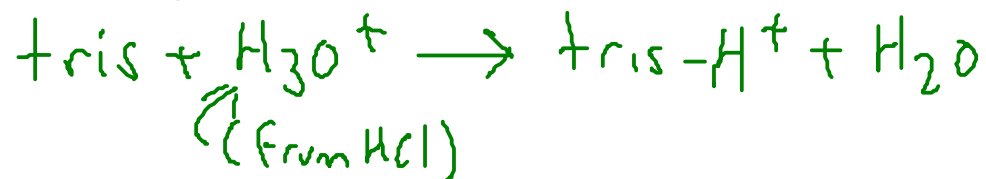Take 100. mL of the previous buffer (0.050 M tris / 0.075 M tris-HCl), and add 5.0 mL of 0.10 M HCl. What is the pH of the mixture?

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

$$tris + H_3O^+ \longrightarrow tris\text{-}H^+ + H_2O$$

(from HCl)

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

Species	Initial mmol	Δ in rxn	Final mmol	[conc.]
tris	100 mL × 0.050 M = 5.0 mmol	−0.5 mmol	4.5 mmol	$\frac{4.5\,mmol}{105\,mL} = 0.0428571\,M$ *
tris-H⁺	100 mL × 0.075 M = 7.5 mmol	+0.5 mmol	8.0 mmol	$\frac{8.0\,mmol}{105\,mL} = 0.0761905\,M$
HCl	5 mL × 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)

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

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...)

$$M_1 V_1 = M_2 V_2$$

$$(0.10 m)(5.0 mL) = M_2 (105 mL)$$

$$0.0047619 m = M_2$$

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

$$[H_3O^+] = 0.0047619 m$$
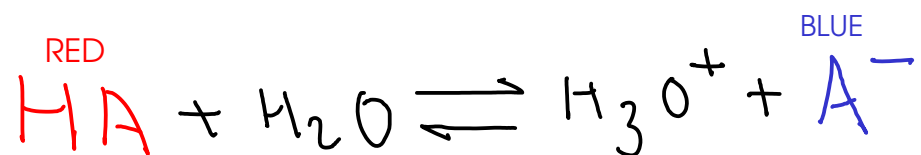
$$\boxed{pH = 2.32}$$

... 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!

$$\underset{\text{RED}}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{\text{BLUE}}{A^-}$$

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

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
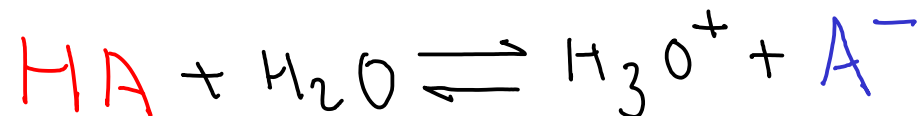
Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

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

When does the color of the indicator change?

IF the pH is << pKa, then the log term above must be both large AND negative!

- What color is the solution?

$$[HA] >> [A^-]$$ ... and the solution is RED.

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

- What color is the solution?

$$[A^-] >> [HA]$$ ... and the solution is BLUE

- 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.

Solubility as an equilibrium process

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
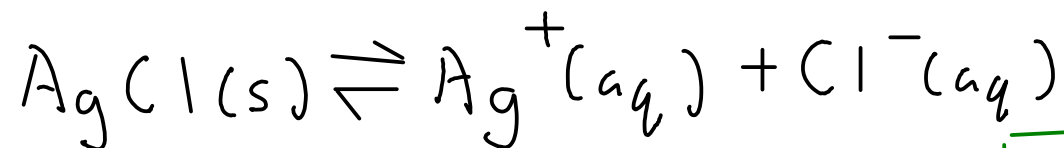possible to dissolve in a given volume of solvent!

A SATURATED SOLUTION is a solution where dissolved solute exists in an
EQUILIBRIUM with undissolved solute!
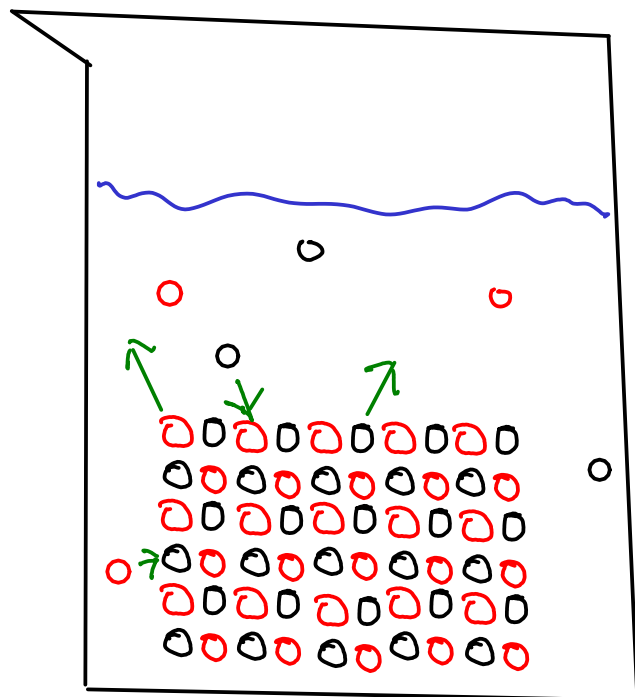
Example: Consider a saturated solution of silver chloride:

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
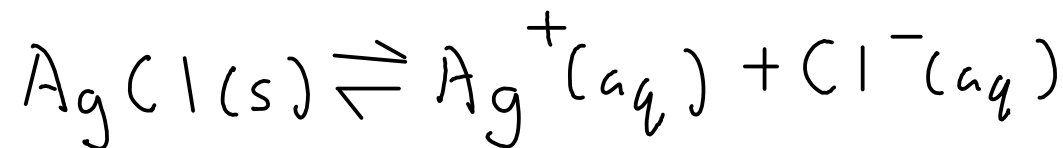
At equilibrium, the rate of dissolving equals the rate of crystallization!

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

$$K_c = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

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

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
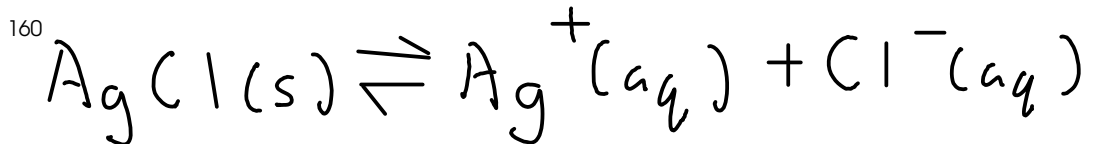
$$K_{sp} = [Ag^+][Cl^-]$$

↪ 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, Ksp 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?

$$Ca_3(PO_4)_2(s) \rightarrow 3Ca^{2+}(aq) + 2PO_4^{3-}(aq)$$

$$K_{sp} = [Ca^{2+}]^3[PO_4^{3-}]^2$$

Solubility calculations and Ksp

You can calculate the solubility of a compound if you know Ksp!

Calculate the solubility (in g/L) of lead(II) iodide at 25C. $FW = 461.0 \ g/mol$
(See Appendix J in OpenStax for solubility product information!)

PbI_2

$Ksp = 1.4 \times 10^{-8} = [Pb^{2+}][I^-]^2$

$PbI_2 \rightleftharpoons Pb^{2+} + 2I^-$
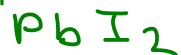
Species	[Initial]	Δ	[Equilibrium]
Pb^{2+}	0	$+X$	X
I^-	0	$+2x$	$2x$

Let "x" equal the change in lead(II) ion concentration ...

$(x)(2y)^2 = 1.4 \times 10^{-8}$

$4x^3 = 1.4 \times 10^{-8}$

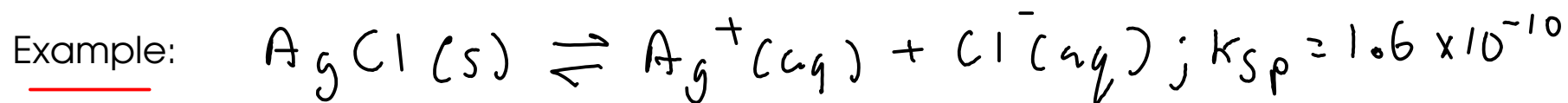$x = 0.0015182945 \ M \ Pb^{2+} = [PbI_2]_{dissolved}$

$\dfrac{0.0015182945 \ mol \ PbI_2}{L} \times \dfrac{461.0 \ g \ PbI_2}{mol \ PbI_2} = 0.70 \ g \ PbI_2/L$

(optional: ppm "parts per million" = mg/L, so $\overline{700}$ ppm PbI_2)

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 Ksp

Example: $AgCl\,(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \,;\, k_{sp} = 1.6 \times 10^{-10}$

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

IF...

$*$ Q < Ksp ; the reaction proceeds to produce more products (dissolved ions), so more solid is able to dissolve: NO PRECIPITATION

$*$ Q > Ksp ; the reaction proceeds to produce more reactants (solid), so solid falls out of solution: PRECIPITATION OCCURS

$*$ Q = Ksp ; the reaction is at equilibrium. PRECIPITATION IS JUST BEGINNING

Would a solution with (Ag+) = 0.014 M and (Cl-) = 0.00042 M precipitate?

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

$$5.88 \times 10^{-6} > 1.6 \times 10^{-10} \,,\, precipitation$$

$$\underset{Q}{} \qquad\qquad \underset{ksp}{}$$

Le Chateleir'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!

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq)$$
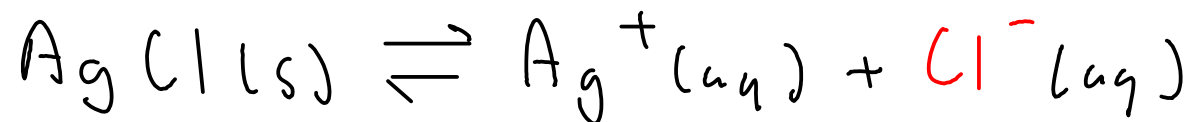
Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

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)

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq); \quad K_{sp} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$
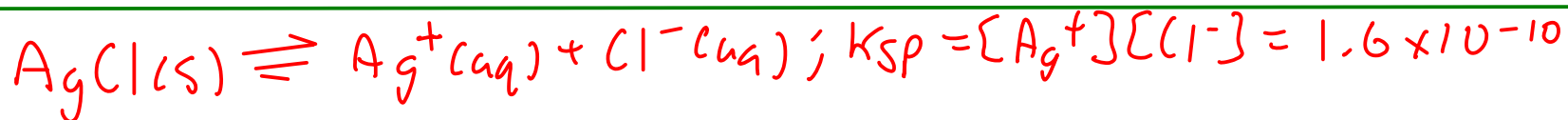
Solve equilibrium...

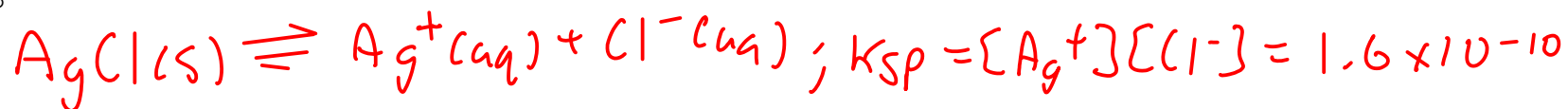| Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	$+x$	x
Cl^-	0	$+x$	x

Let "x" equal the change in silver ion concentration

$$(x)(x) = 1.6 \times 10^{-10}$$

$$x^2 = 1.6 \times 10^{-10}$$

$$x = 1.264911064 \times 10^{-5} M = [Ag^+] = [AgCl]_{dissolved}$$

$$\frac{1.264911064 \times 10^{-5} \, mol \, AgCl}{L} \times \frac{143.35 \, g \, AgCl}{mol \, AgCl} = 0.0018 \, \frac{g \, AgCl}{L} = \boxed{1.8 \, ppm \, AgCl}$$

$$AgCl(s) \rightleftharpoons Ag^+(aq) + Cl^-(aq) \; ; \; K_{SP} = [Ag^+][Cl^-] = 1.6 \times 10^{-10}$$

Now solve for the AgCl dissolved in 0.10 M NaCl

Species	[Initial]	Δ	[Equilibrium]
Ag^+	0	+X	X
Cl^-	0.10	+X	0.10 +X

Let "x" equal the change in silver ion concentration.

$$(x)(0.10 + x) = 1.6 \times 10^{-10}$$
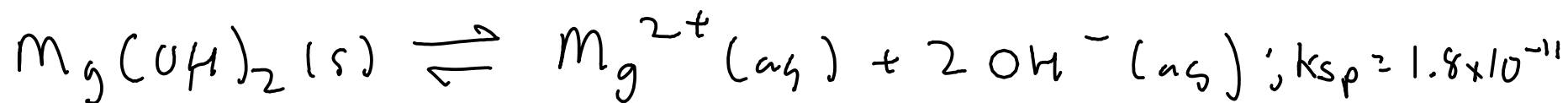
↓ Assume x << 0.10

$$(x)(0.10) = 1.6 \times 10^{-10}$$

$$x = 1.6 \times 10^{-9} = [Ag^+] = [AgCl]_{dissolved}$$

$$\frac{1.6 \times 10^{-9} \text{ mol } Ag Cl}{L} \times \frac{143.35 g \, AgCl}{mol \, AgCl} = 2.3 \times 10^{-7} \frac{g}{L} = \boxed{0.00023 \, ppm \, AgCl}$$

Compare: Solubility in DI water was 1.8 ppm. Solubility in 0.10 M NaCl (common ion, Cl-) is 0.00023 ppm.

Conclusion: The presence of a common ion GREATLY decreases solubility.

pH AND SOLUBILITY

$$Mg(OH)_2 (s) \rightleftharpoons Mg^{2+}(aq) + 2OH^-(aq) \; ; \; k_{sp} = 1.8 \times 10^{-11}$$

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

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