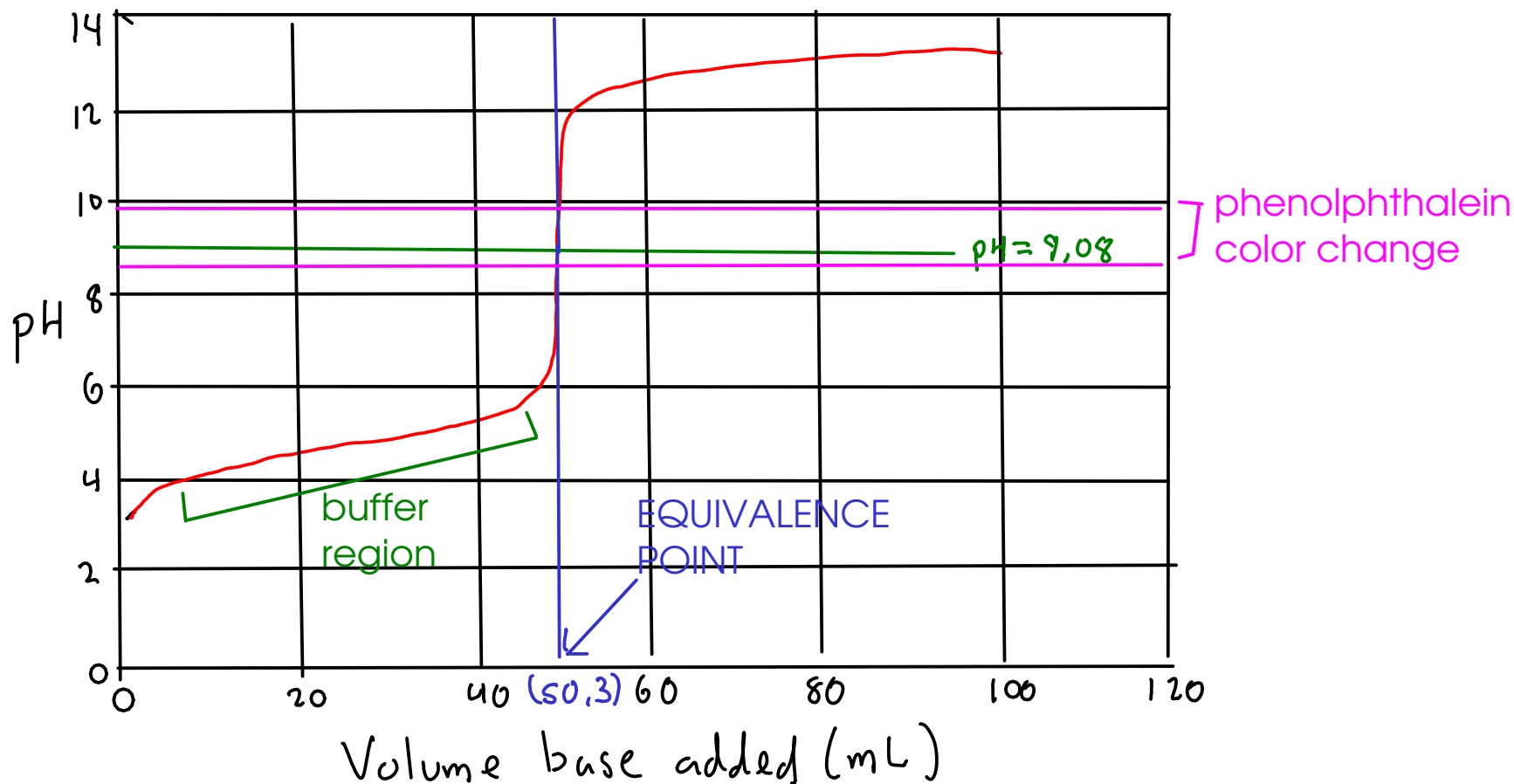


Another interesting point: The halfway point



What's special about it? It's the point where we have added half the required base to reach the equivalence point

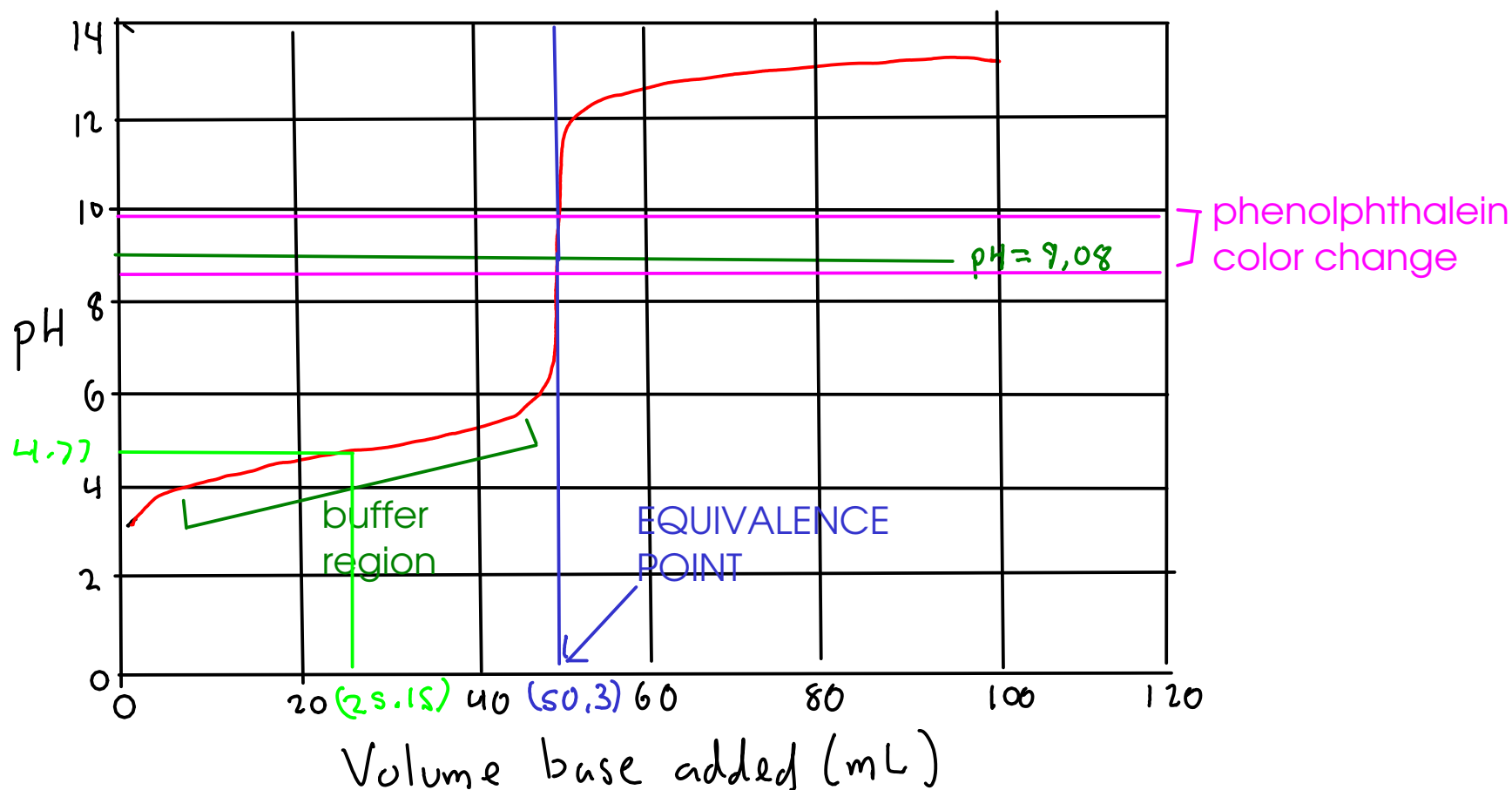


17,6 mmol $\text{HC}_2\text{H}_3\text{O}_2$
initially

Add 25.15 mL base

$$25,15 \text{ mL} \times \frac{.350 \text{ mol}}{\text{L}} = 8,8025 \text{ mmol NaOH}$$

8.8 millimoles is also the amount of acid left, and the added base gets converted to acetate ion!



The total volume is 25.15 mL, and both the acid and base are present at the same concentration. We have a BUFFER.

Find the pH of this buffer using the Henderson-Hasselbalch equation.

$$\text{pH} = \text{p}K_{\text{a}, \text{HC}_2\text{H}_3\text{O}_2} + \log \left(\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

= 0, since the ratio = 1

At the halfway point, the pH = pKa of the acid!

Useful for finding acid ionization constants!

SOLUTION: Homogeneous mixture of substances Solutions contain:

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

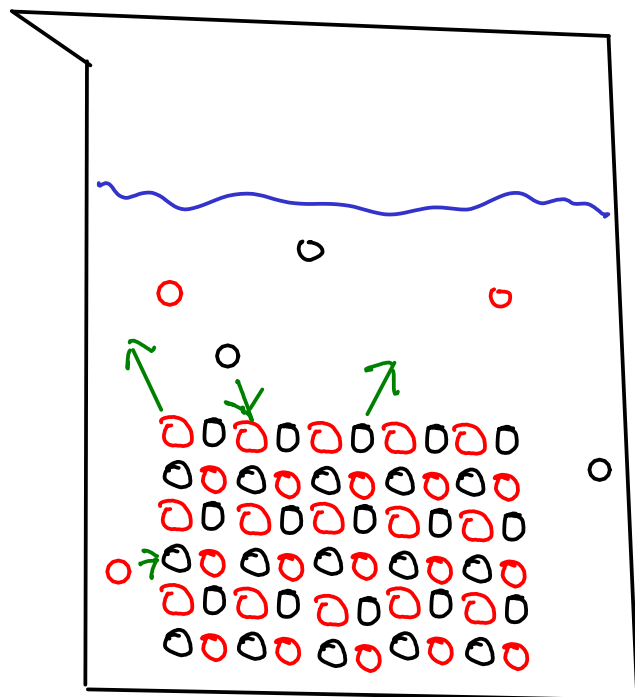
SOLVENT: Component of a solution present in greatest amount

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

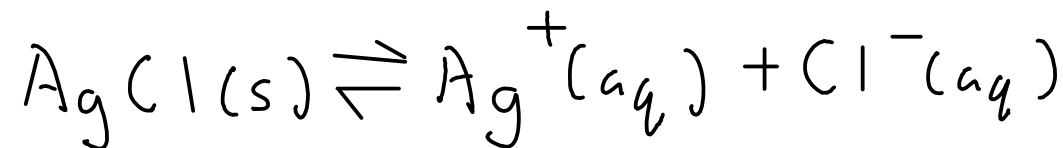
SOLUBILITY: The amount of a solute that will dissolve in a given volume of solvent

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

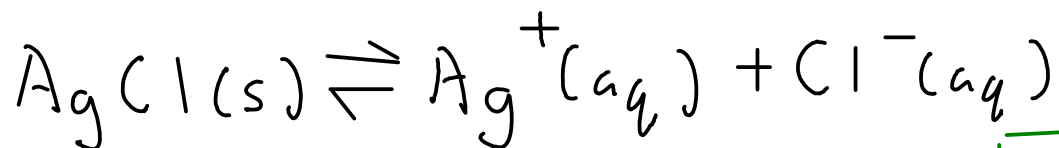
A SATURATED SOLUTION is a solution where dissolved solute exists in an EQUILIBRIUM with undissolved solute!



Example: Consider a saturated solution of silver chloride:

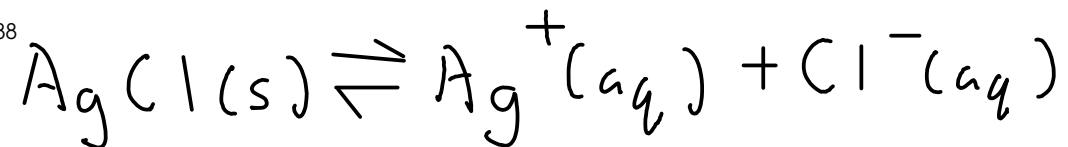


At equilibrium, the rate of dissolving equals the rate of crystallization!



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

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

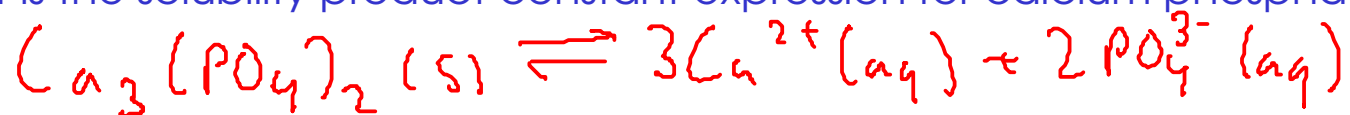


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↪ 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?



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

189 Solubility calculations and K_{sp}

You can calculate the solubility of a compound if you know K_{sp}!

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

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



Species	[Initial]	Δ	[Equilibrium]
Pb^{2+}	0	+x	x
I^{-}	0	+2x	2x

We need to solve this expression to find the solubility.

$(x)(2x)^2 = 6.5 \times 10^{-9}$
 $4x^3 = 6.5 \times 10^{-9}$

$x = 0.0011756673 = [Pb^{2+}] = [PbI_2]_{\text{dissolved}}$

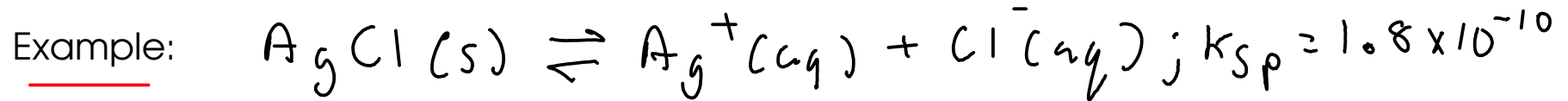
Since the dissolved lead concentration here equals the dissolved lead iodide concentration, we just need to convert units from molarity to mass...

$\frac{0.0011756673 \text{ mol } PbI_2}{L} \times \frac{461.0 \text{ g } PbI_2}{\text{mol } PbI_2} = 0.54 \text{ g/L } PbI_2 = 540 \text{ ppm } PbI_2$

Note: A common solubility unit for "insoluble" compounds is "parts per million" - ppm. ppm for dilute aqueous solutions is equivalent to mg/L

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?

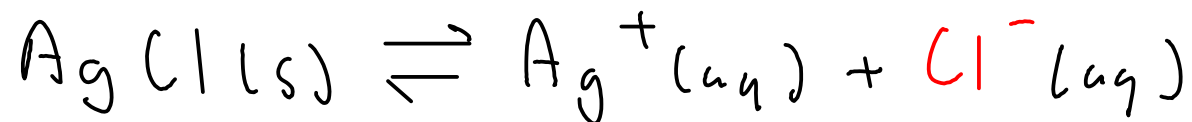
$$Q = [Ag^+][Cl^-] = (0.014)(0.00042) = 5.88 \times 10^{-6}$$

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

Since $Q > K_{sp}$, PRECIPITATION OCCURS!

¹⁹¹ 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!

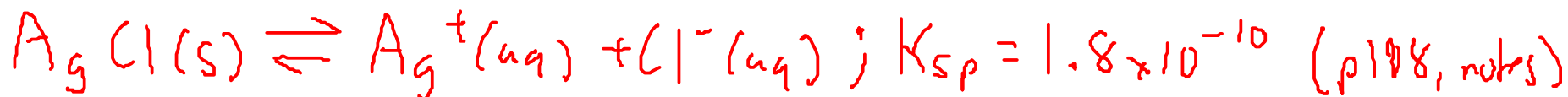


Silver chloride is much less soluble in a solution of 0.1 M NaCl than it is in distilled water. Why? The presence of CHLORIDE ION forces the solubility equilibrium back to the left, meaning less silver chloride can dissolve!

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)



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

For distilled water ...

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

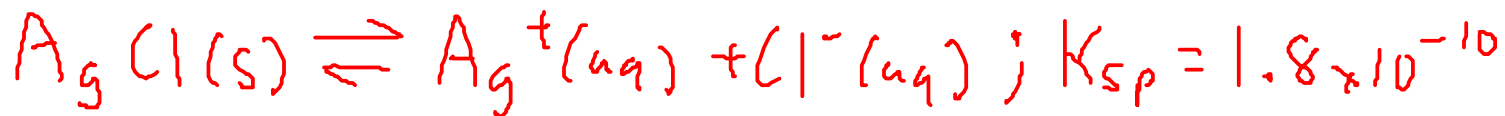
Let 'x' equal the change in silver ion concentration

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

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

We need this in ppm units, so ...

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



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

For 0.10 M NaCl solution ...

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

Let 'x' equal the change in silver ion concentration

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

↓ Assume $x \ll 0.10$, so $0.10+x = 0.10$

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

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

Convert to ppm...

mol \rightarrow g

g \rightarrow mg

$$1.8 \times 10^{-9} \frac{\text{mol AgCl}}{\text{L}} \times \frac{143.35 \text{ g AgCl}}{\text{mol AgCl}} \times \frac{\text{mg}}{10^{-3} \text{ g}} = 2.6 \times 10^{-4} \text{ ppm AgCl} \\ (0.00026) \text{ in } 0.10 \text{ M NaCl}$$

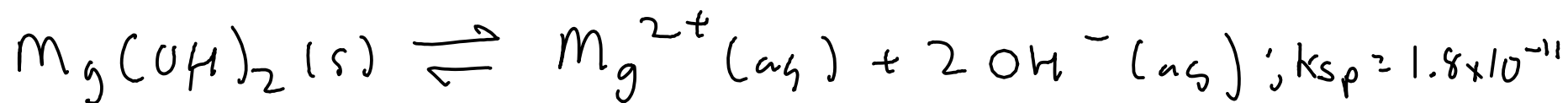
Compare:

1.9 ppm AgCl in distilled water

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

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