

## <sup>168</sup> BUFFER SELECTION

- Buffer pH is controlled by the pKa of the acidic species in the buffer.

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

- Choose a buffer system so that the desired pH is within +/- 1 pH unit of the pKa
- You also need to ensure that the components of the buffer do not interact with your chemistry!

## BUFFER PREPARATION

- many buffers are prepared by mixing specific amounts of both components of the Buffer system (acid / conjugate base or base / conjugate acid)

Some buffer "recipes" call for making the conjugate ion FROM the weak acid or base ... by adding a STRONG acid or base!



The reaction of the strong acid with the weak base goes essentially to completion!

If you have more ammonia than nitric acid, you will end up with a solution containing a significant amount of both ammonia and ammonium ion ... a buffer!

## BUFFER CAPACITY

- A buffer is good only as long as there is a significant concentration of both the acidic and basic species
- buffer capacity: how much acid or base can a buffer resist before losing its ability to buffer
- Buffer pH depends on the RATIO of acid to base!

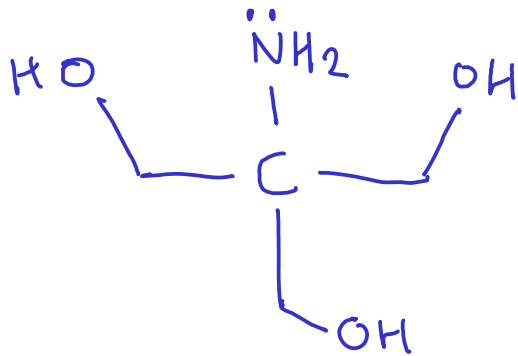
$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log\left(\frac{[\text{basic species}]}{[\text{acidic species}]}\right)$$

Henderson-Hasselbalch Equation

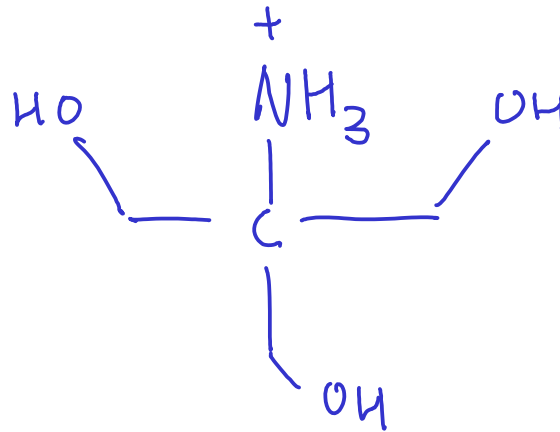
Ratio determines pH; the actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A<sup>-</sup>, it will have the same pH as a buffer with 2.0M HA and 2.0M A<sup>-</sup> .... but the 2M buffer will have a higher BUFFER CAPACITY - it will resist more additions of acid or base.

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



tris base



tris-HCl (conjugate acid of tris base)

$\text{Cl}^-$

$$\text{p}K_a = 8,06$$

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.

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

$$[\text{tris}] : m_1 V_1 = m_2 V_2 \quad (0.10 \text{ M})(50 \text{ mL}) = m_2 (100 \text{ mL})$$

$$m_2 = 0.050 \text{ M tris base}$$

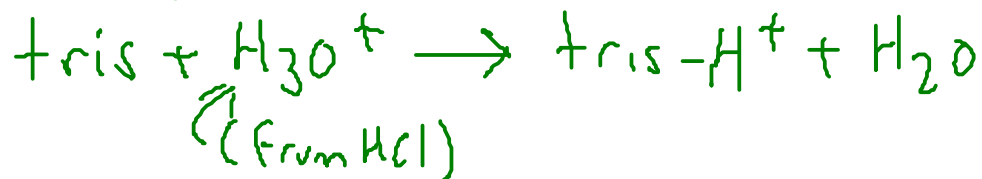
$$[\text{tris-HCl}] : m_1 V_1 = m_2 V_2 \quad (0.15 \text{ M})(50 \text{ mL}) = m_2 (100 \text{ mL})$$

$$m_2 = 0.075 \text{ M tris-HCl}$$

$$\text{pH} = 8.06 + \log \left( \frac{0.050 \text{ M}}{0.075 \text{ M}} \right) = 7.88$$

171 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:

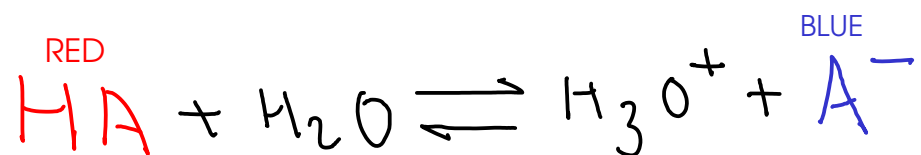
$$[\text{H}_3\text{O}^+] = 0.0047619 \text{ M}$$

$$\text{pH} = 2.32$$

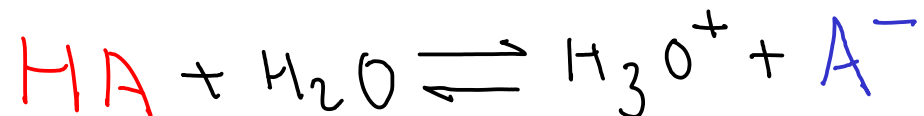
... which is a change of 4.68 pH units from water's original pH of 7.00!

## 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

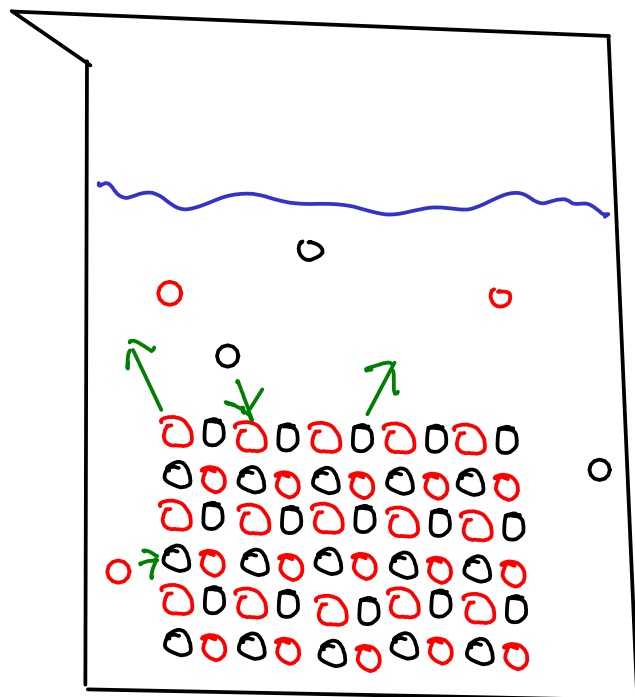
We usually call water the solvent in aqueous mixtures, even if the water is present in smaller amount than another component

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

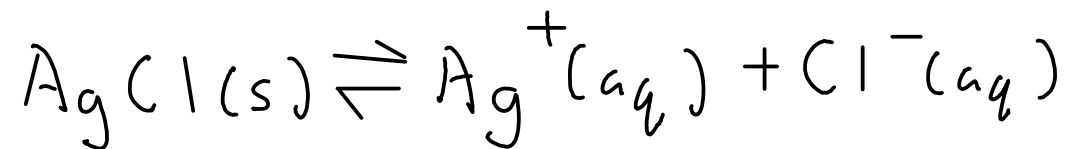
SATURATED SOLUTION: Contains the maximum amount of solute that it is possible to dissolve in a given volume of solvent!

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

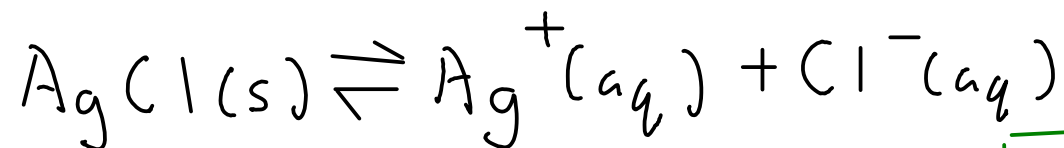




Example: Consider a saturated solution of silver chloride:

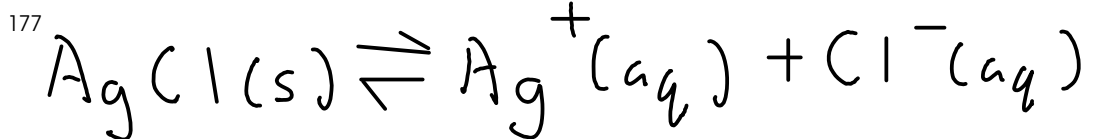


At equilibrium, the rate of dissolving equals the rate of crystallization!



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

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

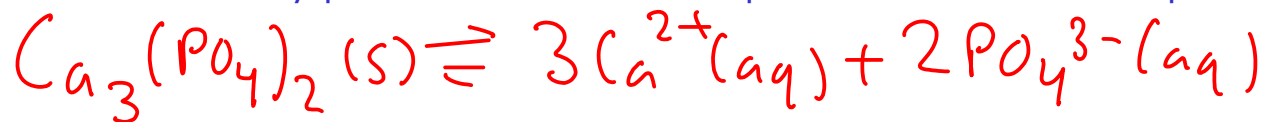


$$K_{sp} = [\text{Ag}^+][\text{Cl}^-]$$

↪ 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?



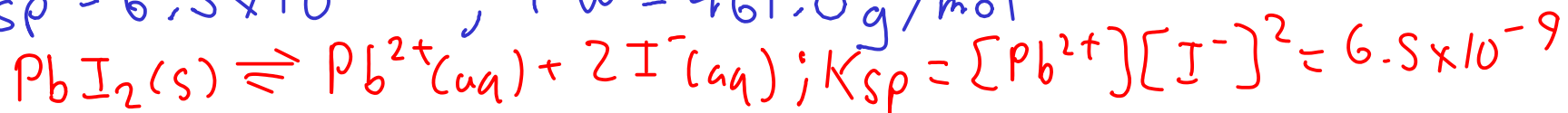
$$K_{sp} = [\text{Ca}^{2+}]^3[\text{PO}_4^{3-}]^2$$

178 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)

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



Set up an equilibrium chart and solve!

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

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

This will ALSO equal the concentration of lead(II) iodide that DISSOLVES.

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

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

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

We have the (molar) solubility, so we need to convert to mass units.

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

$\rightarrow 540 \text{ ppm } PbI_2$

ppm = "parts per million" - a common solubility unit that's equivalent to mg/L