THE COMMON-ION EFFECT

- is the effect on the ionization of a compound caused by the presence of an ion involved in the equilibrium

- is essentially Le Chateleir's Principle applied to equilibria involving ions

ex: $NH_3(aq) + H_2O(l) \rightleftharpoons NH_4^+(aq) + OH^-(aq)$; $K_b = 1.8 \times 10^{-5}$

From previous calculations, we know that an 0.10 M solution of ammonia has a pH of 11.13 .

What would happen to the pH if we dissolved ammonium chloride into the solution?

$NH_4Cl(s) \longrightarrow NH_4^+(aq) + Cl^-(aq)$

The ammonium chloride provides the ammonium ion. According to Le Chateleir's principle, this would shift the ammonia equilibrium to the LEFT!

What would happen to the pH? Let's find out!

Calculate the pH of a solution which contans 0.10 M ammonia AND 0.10 M ammonium chloride.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; \; Kb = 1.8 \times 10^{-5} \quad (p\,A-14, E+G)$$

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8 \times 10^{-5}$$

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

Species	[Initial]	Δ	[Equilibrium]
NH_4^+	0.10	$+X$	$0.10 + X$
OH^-	0	$+X$	X
NH_3	0.10	$-X$	$0.10 - X$

$$\frac{(0.10 + x)(x)}{(0.10 - x)} = 1.8 \times 10^{-5}$$

Assume x is small compared to 0.10, so 0.10 -x = 0.10 , and 0.10 + x = 0.10

$$\frac{0.10 \, x}{0.10} = 1.8 \times 10^{-5}$$

$$X = 1.8 \times 10^{-5} = [OH^-]$$

$$pOH = 4.74$$

$$pH = 14.00 - 4.74$$

$$\boxed{pH = 9.26}$$

(The pH of the 0.10 M ammonia-only solution was 11.13…)

BUFFERS

- resist pH change caused by either the addition of strong acid/base OR by dilution

Made in one of two ways:

$HC_2H_3O_2$ $NaC_2H_3O_2$

① Make a mixture of a weak acid and its conjugate base (as the SALT)

NH_3 NH_4Cl

② Make a mixture of a weak base and its conjugate acid (as the SALT)

For a weak acid, you would:

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$

- Add HA (weak acid)
- Add a salt containing A^- (example: NaA)

- This solution actually contains an acid and a base at equilibrium, with a significant concentration of BOTH.

- The acid in the buffer can neutralize bases, while the base can neutralize acids.

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
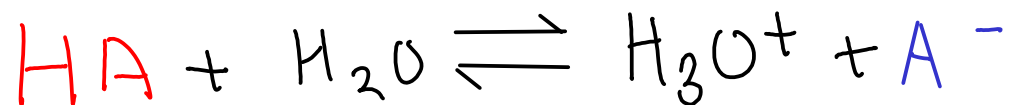
$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

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

Henderson-Hasselbalch Equation

$[A^-]$ ... from the salt

$[HA]$ ... from the weak acid

- We ASSUME that the initial concentrations of both the acid and its conjugate are equal to the equilibrium concentrations. Valid IF there are significant amounts of both species initially.

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

Henderson-Hasselbalch Equation

ex: acidic buffer

$HC_2H_3O_2 \,/\, NaC_2H_3O_2$

$$pH = pK_{a,\,HC_2H_3O_2} + \log\left(\frac{[C_2H_3O_2^-]}{[HC_2H_3O_2]}\right)$$

ex: basic buffer

$NH_3 \,/\, NH_4NO_3$

$$pH = pK_{a,\,NH_4^+} + \log\left(\frac{[NH_3]}{[NH_4^+]}\right)$$

$pK_a + pK_b = 14.00$ ... is the -log of $K_a \times K_b = K_w$

Calculate the pH of a buffer made from 30.2 grams of ammonium chloride (FW = 53.492 g/mol) and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

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

Henderson-Hasselbalch Equation

$[NH_3] = ?$ $M_1 V_1 = M_2 V_2$ $(18.1m)(29mL) = M_2(150.mL)$

$M_2 = 3.499333333 \, m \, NH_3$

$[NH_4^+] = ?$ $30.2 \, g \, NH_4Cl \times \frac{mol \, NH_4Cl}{53.492 \, g \, NH_4Cl} = 0.564570403| \, mol \, NH_4^+$

$[NH_4^+] = \dfrac{0.564570403| \, mol \, NH_4^+}{0.150L} = 3.763802687 \, M \, NH_4^+$

$pK_{a, NH_4^+} = ?$ $K_{b, NH_3} = 1.8 \times 10^{-5}$ $(pA - 14) ; pK_b = 4.74$

$pK_a + pK_b = 14.00$, so $pK_a = 9.26$

$$pH = 9.26 + \log\left(\frac{3.499333333 \, M \, NH_3}{3.763802687 \, M \, NH_4^+}\right)$$

$= 9.26 + -0.03164 = \boxed{9.23}$

BUFFER SELECTION

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

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

- 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 / conuugate acid)

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

$$NH_3 + HNO_3 \longrightarrow NH_4^+ + NO_3^-$$

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!

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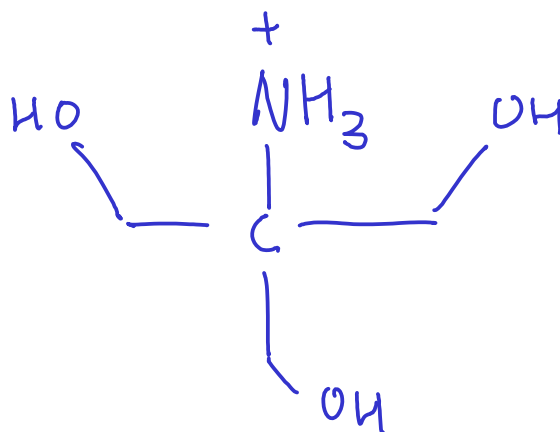
Henderson-Hasselbalch Equation

Ratio determines pH; the actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A- , it will have the same pH as a buffer with 2.0M HA and 2.0M A- .... 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
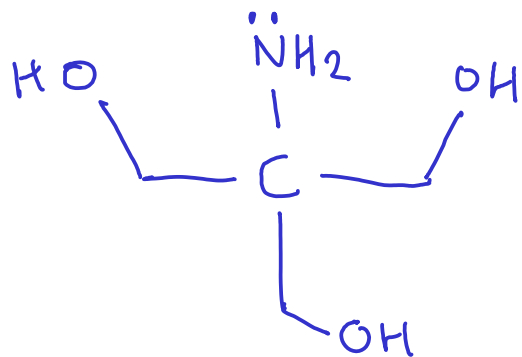
tris base

tris-HCl (conjugate acid of tris base)

$pKa = 8.06$

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.

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

$[tris]$: $M_1 V_1 = M_2 V_2$ $(0.10m)(50.mL) = M_2(100.mL)$

$M_2 = 0.050 \, M \, tris$

$[tris-HCl]$: $(.15m)(50.mL) = M_2(100.mL)$

$M_2 = 0.075 \, M \, tris-HCl$

$$pH = 8.06 + \log\left(\frac{.050}{0.075}\right) = \boxed{7.88}$$

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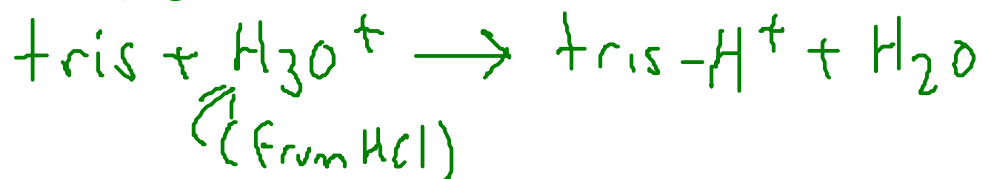
... so we need to find out the NEW concentrations of each species in the system.

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

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

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...)

$$M_1 V_1 = M_2 V_2$$

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

$$0.0047619 \, m = M_2$$

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!

RED

BLUE

$$HA + H_2O \rightleftharpoons H_3O^+ + A^-$$
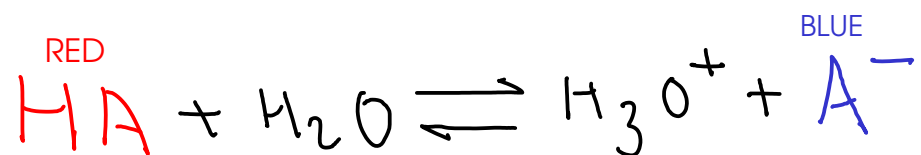
The indicator must be present in very low concentrations - so that the indicator's equilibrium DOES NOT CONTROL the pH of the solution!

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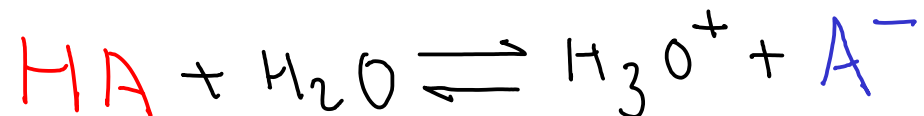
Look at the Henderson-Hasselbalch equation - we want to know how much of the red form and how much of the blue form are present!

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

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.