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

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; K_b = \frac{[NH_4^+][OH^-]}{[NH_3]} = 1.8\times10^{-5}$$

(pA-14)

As we did with the solution that only contained ammonia initially, set up an equilibrium chart!

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

Let "x' equal the increase in ammonium ion concentration...

Plug back into equilibrium expression ...

$$\frac{(0.10+x)(x)}{(0.10-x)} = 1.8\times10^{-5}$$

If we assume x is much smaller than 0.10, then ...
0.10 - x = 0.10 AND
0.10 + x = 0.10

$$\frac{0.10x}{0.10} = 1.8\times10^{-5}$$

$$x = 1.8\times10^{-5}$$

$x = 1.8\times10^{-5} = [OH^-]$

$pOH = 4.74$, and

$pH = 14.00 - 4.74 = \boxed{9.26}$

For comparison,
pH of 9.26 is still basic, but the pH of the ammonia-only solution is MORE basic (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.

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

ex: acidic buffer

$HC_2H_3O_2$ / $NaC_2H_3O_2$

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

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ex: basic buffer

NH_3 / NH_4NO_3

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

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

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.

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

Henderson-Hasselbalch Equation

$[NH_3]$: Ammonia was diluted ... use M1V1=M2V2

$$\underset{M_1}{(29\,mL)}\,\underset{V_1}{(18.1\,M)} = M_2\,\underset{V_2}{(150.\,mL)} \;;\; M_2 = 3.499333333\,M\ NH_3$$

$[NH_4^+]$: DIssolved solid ammonium chloride into 150 mL volume. Find moles of solid!

$$30.2\,g\ NH_4Cl \times \frac{mol\ NH_4Cl}{53.492\,g\ NH_4Cl} = 0.564570403\,mol\ NH_4Cl$$

$$\frac{0.564570403\,mol\ NH_4^+}{0.150\,L} = 3.763802687\,M\ NH_4^+$$

pK_a: $K_{a,NH_4^+} = ?$ $K_{b,NH_3} = 1.8\times10^{-5}$; $pK_b = 4.74$

Since $pK_a + pK_b = 14$, $pK_a + 4.74 = 14$, $pK_a = 9.26$

Use H-H instead of equilibrium chart ...

$$pH = 9.26 + \log\left(\frac{3.499333333\,M\ NH_3}{3.763802687\,M\ NH_4^+}\right) = \boxed{9.22}$$