Solve the equilibrium of phosphoric acid's FIRST proton:

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+ \; ; K_{a_1} = 6.9 \times 10^{-3}$

$$K_a = \frac{[H_2PO_4^-][H_3O^+]}{[H_3PO_4]} = 6.9 \times 10^{-3}$$

Species	[Initial]	Δ	[Equilibrium]
H_3PO_4	0.10	$-x$	$0.10 - x$
$H_2PO_4^-$	0	$+x$	x
H_3O^+	0	$+x$	x

$$\frac{x^2}{0.10 - x} = 6.9 \times 10^{-3}$$

This time, we'll solve the quadratic equation. We're not quite as confident that 'x'<<0.10 as we were in previous examples. (The equilibrium constant is a good bit larger here!)

$x^2 = 0.00069 - 0.0069x$

$x^2 + 0.0069x - 0.00069 = 0$

$a = 1 \quad b = 0.0069 \quad c = -0.00069$

$$x = \frac{-0.0069 \pm \sqrt{(0.0069)^2 - 4(1)(-0.00069)}}{2(1)}$$

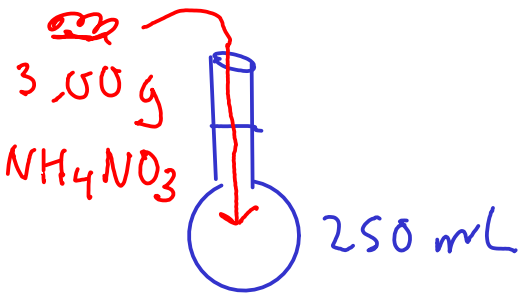
$$x = \frac{-0.0069 \pm 0.052986886852}{2}$$

Discard the negative root. 'x' can't be less than zero (it's equal to two of the concentrations!)

$x = 0.0230 = [H_3O^+]$

$\boxed{pH = 1.64}$

Find the pH of a solution prepared by dissolving 3.00 g of ammonium nitrate solid into enough water to make 250. mL of solution.



NH_4NO_3: N : 2 × 14.01
H : 4 × 1.008
O : 3 × 16.00
80.052 g NH_4NO_3 = 1 mol NH_4NO_3

Find out the nature of the salt: Acidic, basic, or neutral.

$NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

$NO_3^- + H_2O \rightleftharpoons \boxed{HNO_3} + OH^-$ ... but niric acid is a STRONG ACID, so NITRATE ION will be neutral.

$NH_4^+ + H_2O \rightleftharpoons \boxed{NH_3} + H_3O^+$ ... ammonia is a WEAK BASE (exists as molecules in solution), so we expect AMMONIUM ION to be acidic.

$NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

$K_{a,NH_4^+} = \dfrac{[NH_3][H_3O^+]}{[NH_4^+]}$

$K_{a,NH_4^+} = ?$

$K_{b,NH_3} = 1.8 \times 10^{-5}$ (p. A-14)

$(K_{a,NH_4^+})(K_{b,NH_3}) = 1.0 \times 10^{-14}$

$K_{a,NH_4^+} = 5.56 \times 10^{-10}$

$$K_{a,NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.56 \times 10^{-10}$$

Species	[Initial]	Δ	[Equil]
NH_3	0	+x	0
H_3O^+	0	+x	0
NH_4^+	0.14990	−x	0.14990 − x

Calculate the initial ammonium nitrate concentration

$$3.00\,g\,NH_4NO_3 \times \frac{mol}{80.052\,g} =$$

$$= 0.037478640\,6\,mol\,NH_4NO_3$$

Concentration:

$$\frac{0.037478640\,6\,mol\,NH_4NO_3}{0.250\,L} =$$

$$= 0.149902563\,3\,M$$

Solve:

$$\frac{x^2}{0.14990 - x} = 5.56 \times 10^{-10}$$

$$\downarrow \quad x \ll 0.14990$$

$$\frac{x^2}{0.14990} = 5.56 \times 10^{-10}$$

$$x = 9.129 \times 10^{-6} = [H_3O^+]$$

$$\boxed{pH = 5.04}$$

This seems reasonable for an acidic salt.

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?

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

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.

$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; \; K_b = 1.8 \times 10^{-5}$

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

Species	[Init]	Δ	[Equil]
NH_3	0.10	$-x$	$0.10 - x$
NH_4^+	0.10	$+x$	$0.10 + x$
OH^-	0	$+x$	x

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

Assume x is small relative to 0.10

$0.10 + x \approx 0.10$

$0.10 - x \approx 0.10$

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

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

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

$pOH = -\log_{10}(1.8 \times 10^{-5}) = 4.74$

$\boxed{pH = 9.26}$

The common-ion effect lowers the pH by suppressing the ionization of the ammonia.

Compare pH: 9.23 vs 11.13

BUFFERS

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

Made in one of two ways:

1. Make a mixture of a weak acid ($HC_2H_3O_2$) and its conjugate base ($NaC_2H_3O_2$) (as the SALT)
2. Make a mixture of a weak base (NH_3) and its conjugate acid (NH_4Cl) (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

$HC_2H_3O_2 / NaC_2H_3O_2$

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

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ex: basic buffer

NH_3 / NH_4NO_3

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

$pK_a + pK_b = 14{,}00$ ... is the -log of $K_a \times K_b = K_w$