POLYPROTIC ACIDS

Find pH of 0,10 M H_3PO_4

... what's special about phosphoric acid?

① $H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$

② $H_2PO_4^- + H_2O \rightleftharpoons HPO_4^{2-} + H_3O^+$

③ $HPO_4^{2-} + H_2O \rightleftharpoons PO_4^{3-} + H_3O^+$

Phosphoric acid has THREE acidic protons!

$K_{a1} = 6,9 \times 10^{-3}$

$K_{a2} = 6,2 \times 10^{-8}$

$K_{a3} = 4,8 \times 10^{-13}$

The first dissocation is dominant here, and for simple calculations of phosphoric acid in water, we will simply use the first ionization and ignore the other two.

Remember: This is a weak acid. It exists in water mostly as undissociated phosphoric acid molecules.

Solving the equilibrium of phosphoric acid's first proton:

$$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$$

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

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
H_3O^+	0	$+x$	x
$H_2PO_4^-$	0	$+x$	x
H_3PO_4	0.10	$-x$	$0.10 - x$

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

This time, let's solve the quadratic equation.
'x'<<0.10 might not be valid here

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

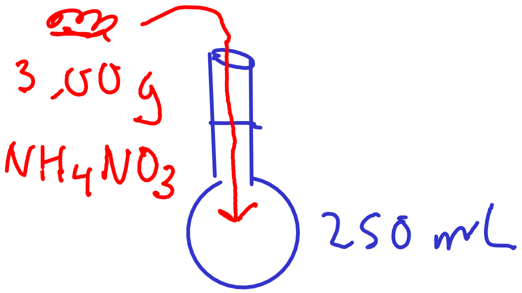
$$x^2 + (6.9 \times 10^{-3})x - (6.9 \times 10^{-4}) = 0$$

$$a = 1, \quad b = 6.9 \times 10^{-3}, \quad c = -6.9 \times 10^{-4}$$

$$x = 2.3043 \times 10^{-2} \ \underline{\underline{OR}} \ -\cancel{2.9943 \times 10^{-2}}$$

$$x = 2.3043 \times 10^{-2} = [H_3O^+], \text{ so } \boxed{pH = 1.64}$$

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 x 14.01

H : 4 x 1.008

O : 3 x 16.00

80.052 g NH_4NO_3 = 1 mol NH_4NO_3

Find out what kind of salt we have - acidic, basic, neutral:

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

$$NO_3^- + H_2O \rightleftharpoons HNO_3 + OH^-$$

Nitric acid is a STRONG ACID, so nitrate ion is a NEUTRAL ion

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

Ammonia is a WEAK BASE, so ammonium ion should be ACIDIC

So, we solve the equilibrium between ammonium ion and water:

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

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

K_a:

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

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

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

$$K_{a,NH_4^+} = \frac{[NH_3][H_3O^+]}{[NH_4^+]} = 5.56\times10^{-10}$$

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
H_3O^+	0	$+x$	x
NH_3	0	$+x$	x
NH_4^+	0.1499	$-x$	$0.1499-x$

Figure out the initial ammonium ion concentration (same as the nominal ammonium nitrate concentration)

$$3.00\,g\ NH_4NO_3 \times \frac{mol}{80.052\,g} = 0.0375\,mol$$

$$\frac{0.0375\,mol}{0.250\,L} = 0.1499025633\,M$$

Solve ...

$$\frac{x^2}{0.1499-x} = 5.56\times10^{-10}$$

$$\Big\downarrow\ x \ll 0.1499$$

$$\frac{x^2}{0.1499} = 5.56\times10^{-10}$$

$$x = 9.13\times10^{-6} = [H_3O^+]$$

$$\boxed{pH = 5.04}$$

(This pH seems reasonable for a salt we expect to be acidic!)

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?

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

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.

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

SPECIES	INITIAL CONC	CHANGE	EQUILIBRIUM CONC
OH^-	0	+ X	X
NH_4^+	0.10	+ X	0.10 + X
NH_3	0.10	− X	0.10 − x

$$K_b = \frac{[NH_4^+][OH^-]}{[NH_3]}$$

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

If we assume 'x'<<0.10, then:

$0.10 - x \simeq 0.10$

$0.10 + x \simeq 0.10$

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

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

$pOH = 4.74$

$pH = 14.00 - 4.74$

$$\boxed{pH = 9.26}$$

The common ion effect suppresses the ionization of amnnoia, LOWERING the pH relative to the original ammonia solution!

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 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

Acid: NH_4^+ Base: NH_3 $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$

We need to find the concentrations of both ammonia (base) and ammoniu,m ion (acid)

$[NH_3]$: $M_1V_1 = M_2V_2$

$(18.1\,M)(29\,mL) = M_2(150.\,mL)$

$M_2 = 3.499\,M\ NH_3O$

$[NH_4^+]$: NH_4Cl: N: 14.01 × 1

H: 1.008 × 4

Cl: 35.45 × 1

53.492 g/mol

$NH_4Cl \rightarrow NH_4^+ + Cl^-$

$$30.2\,g\ NH_4Cl \times \frac{mol}{53.492\,g} \times \frac{}{0.150\,L} = 3.764\ \underline{M}\ NH_4^+$$

$K_{b,NH_3} = 1.8\times10^{-5}$; $pK_b = 4.74$; $pK_a = 14.00 - 4.74 = 9.26$

$$pH = 9.26 + \log\left(\frac{3.499}{3.764}\right) = \boxed{9.23}$$