0.100 M $NaC_2H_3O_2$, Find pH

$$NaC_2H_3O_2 \rightarrow Na^+ + C_2H_3O_2^-$$

Check the ions formed when sodium acetate dissolves.

Na^+: Not a B-L acid (no H to donate). Not likely to be a B-L base, since it's a positively charged alkali metal ion.

$C_2H_3O_2^-$: Has hydrogen atoms, but not likely to be an acid. It's got a negative charge and the hydrogen atoms are bonded to carbon rather than oxygen. It's ,more likely be a base - a proton acceptor!

$$C_2H_3O_2^- + H_2O \rightleftharpoons \underbrace{HC_2H_3O_2} + OH^-$$

Acetic acid. Since acetic acid is a WEAK ACID, it's stable in water. We expect the ACETATE ION to function as a base.

$$K_{b,C_2H_3O_2^-} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]}$$

Kb for acetate ion is not available in the chart on page A-14 ... BUT we can find the Ka for acetic acid - its conjugate - on the previous page

$K_{a,HC_2H_3O_2} = 1.7 \times 10^{-5}$; $K_aK_b = 1.0 \times 10^{-14}$; $K_b = 5.88 \times 10^{-10}$

$$K_{b,C_2H_3O_2^-} = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.88\times10^{-10}$$

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^-$$

Species	[Initial]	Δ	[Equlibrium]
$HC_2H_3O_2$	0	$+x$	x
OH^-	0	$+x$	x
$C_2H_3O_2^-$	0.100	$-x$	$0.100-x$

$$\frac{x^2}{0.100-x} = 5.88\times10^{-10}$$

$\downarrow$ $x \ll 0.100$

$0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 5.88\times10^{-10}$$

$x = 7.67\times10^{-6} = [OH^-]$

We need pH, but we have the HYDROXIDE concentration!

$pOH = -\log_{10}(7.67\times10^{-6})$

$pOH = 5.12$

Convert to pH:

pH + pOH = 14.00

$\boxed{pH = 8.88}$

Compare:

pH = 7.00 for pure distilled water

pH = 11.12 for 0.100 M ammonia (weak base)

pH = 13.00 for 0.100 M NaOH (strong base)

0.100 M NaCl, Find pH

$$NaCl \rightarrow Na^+ + Cl^-$$

Check the ions formed to see if they're acidic or basic:

Na^+ : Not a B-L acid (no H to donate), and unlikely to ne a B-L base due to it being a small, positively charged alkali metal.

Cl^- ; Not a B-L acid (no H to donate), but may be a B-L base

$$Cl^- + H_2O \rightleftharpoons \underbrace{HCl} + OH^-$$

Hydrochloric acid (HCl) is a STRONG ACID, so it doesn't exist as a stable molecule in water. So, CHLORIDE ION must not function as a base - it's not a good proton acceptor.

Since neither sodium ion nor chloride ion affect the pH, the pH is set by the water equilibrium. The pH will be 7.00 (just as it would be for distilled water)

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.

Solve the equilibrium of phosphoric acid's FIRST proton:

$H_3PO_4 + H_2O \rightleftharpoons H_2PO_4^- + H_3O^+$; $Ka_1 = 6,9 \times 10^{-3}$

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

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!)

$$x^2 = 0,00069 - 0,0069x$$

$$x^2 + 0,0069x - 0.00069 = 0$$

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

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

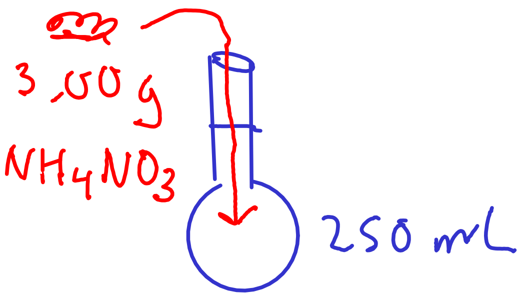
$$x = \frac{-0,0069 \pm 0.0529868852}{2}$$

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 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 the nature of this salt:

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

$$NO_3^- + H_2O \rightleftharpoons \boxed{HNO_3} + OH^-$$

Nitric 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, so AMMONIUM ION is ACIDIC!

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

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

K_{a,NH_4^+}

$K_{b,NH_3} = 1.8 \times 10^{-5}$

Since $K_a \cdot K_b = 1.0 \times 10^{-14}$

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

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

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

Calculate molar concentration of ammonium nitrate:

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

$$= 0.374756408\ mol$$

$$\frac{0.374756408\ mol}{0.250\,L} =$$

$$= 0.149902563\ \underline{M}\ NH_4NO_3$$

Solve:

$$\frac{x^2}{0.14990 - x} = 5.56\times10^{-10}$$

$x \ll 0.14990$

$$\downarrow$$

$$\frac{x^2}{0.14990} = 5.56\times10^{-10}$$

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

$$\boxed{pH = 5.04}$$

This pH 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?

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

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.

$$NH_3 + H_2O \rightleftharpoons NH_4^+ + OH^- \; ; \; K_b = 1{,}8\times10^{-5}$$

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

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

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

Assume x is small compared to 0.10

$$0{,}10 + x \approx 0{,}10$$
$$0{,}10 - x \approx 0{,}10$$

$$\frac{0{,}10x}{0{,}10} = 1{,}8\times10^{-5}$$

$$x = 1{,}8\times10^{-5} = [OH^-]$$

$$pOH = -\log_{10}(1{,}8\times10^{-5}) = 4.74$$

$$\boxed{pH = 9.26}$$

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