0.100 M $NaC_2H_3O_2$, Find pH

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

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

Na^+: Can't donate a proton (no H), Not likely to acccept proton due to positive charge, so sodium ion is probably neutral.

$C_2H_3O_2^-$: Possibly a base? Let' check: $C_2H_3O_2^- + H_2O \rightleftharpoons \boxed{HC_2H_3O_2} + OH^-$

acetic acid is a WEAK acid, meaning it's water-stable and that acetate ion can hold on to protons!

Since acetate ion is basic, we'll solve the equilibrium of acetate ion in water.

$$C_2H_3O_2^- + H_2O \rightleftharpoons HC_2H_3O_2 + OH^- \; ; \; Kb = \frac{[HC_2H_3O_2^-][OH^-]}{[C_2H_3O_2^-]}$$

... but what is the value of Kb? The chart (page A-14) does not list a Kb value for acetate ion. Instead, the charts list Ka for the conjugate acid ... acetic acid. We'll need to use a pH identity to convert from Ka of acetic acid to Kb of acetate ion.

For a conjugate pair, $Ka \times Kb = 1.00 \times 10^{-14}$ $\quad Ka_{,HC_2H_3O_2} = 1.7 \times 10^{-5}$

$$(1.7 \times 10^{-5})Kb = 1.00 \times 10^{-14}$$

$$Kb = 5.88 \times 10^{-10}$$

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

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

Let "x" equal the change in HYDROXIDE ION concentration...

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

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

Assume x << 0.100, so 0.100-x = 0.100

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

$$x = 7.67\times10^{-6}$$

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

$$pOH = 5.12$$

$$\boxed{pH = 8.88}$$

$$pOH = -\log_{10}[OH^-]$$

$$pH + pOH = 14.00$$

For comparison:

0.100 M sodium acetate, pH = 8.88

0.100 M ammonia, pH = 11.13

0.100 M NaOH (strong base), pH = 13.00

The acetate ion is basic, but it's a very weak base!

0.100 M NaCl, Find pH

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

Na^+: Cannot be a Bronsted acid, as it's got no hydrogen to donate. Not a likely base either, due to the positive charge, Neutral.

Cl^-: Can't be an acid, but can it be a base? Check: $Cl^- + H_2O \rightleftharpoons \boxed{HCl} + OH^-$

HCl is strong, meaning complete ionization in water. HCl is NOT water-stable, so chloride ion can't accept protons!

... chloride ion is ALSO neutral!

Since neither sodium nor chloride ions affect pH, the pH of a NaCl solution is set by water itself ... and is 7.00.

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:

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

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

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

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

assume $x \ll 0.10$

so $0.10 - x \simeq 0.10$

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

$$x = 0.026267851 = [H_3O^+]$$

So, $pH = -\log(0.026267851)$

$$\boxed{pH = 1.58}$$

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.

(pA-14)

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

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...

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

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

Assume x << 0.10, so
0.10 - x = 0.10
0.10 + x = 0.10

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

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

$pOH = 4.74$ $\quad pOH = \log_{10}[OH^-]$

$\boxed{pH = 9.26}$ $\quad pH + pOH = 14.00$

Compared to 0.10 M ammonia, the pH of the mixture of ammonia/ammonium chloride is LOWER. Why?

1) Ammonium ion is acidic!
2) Ammonium ion causes the equilibrium to shift LEFT, reducing HYDROXIDE concentration ... meaning water makes more HYDRONIUM!

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.