$0.100\ M\ NaC_2H_3O_2$, Find pH

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

Check the ions formed by the salt to see if they have acidic or basic properties.

Na^+: Not B-L acid, since there is no H+ to donate. Not likely to be B-L base due to the positive charge ... which would repel H+

$C_2H_3O_2^-$: This species does have hydrogen atoms, but it's more likely to be a B-L base due to the negative charge. (Would attract H+)

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

ACETIC ACID: This is a WEAK ACID, meaning that it's stable in water. Since the product of the reaction is stable in water, we expect acetate ion to function as a base.

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

Value for Kb? As before, we don't find a Kb for acetate in our chart on A-14, so we look for a Ka for the conjugate - acetic acid.

$$K_{a,HC_2H_3O_2} = 1.7 \times 10^{-5};\ \text{so } K_b = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.89 \times 10^{-10}$$

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

$$K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = 5.89 \times 10^{-10}$$

Now, we set up and solve this B-L BASE equilibrium to find the pH

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

$$\frac{(x)(x)}{0.100 - x} = 5.89 \times 10^{-10}$$

$$\frac{x^2}{0.100 - x} = 5.89 \times 10^{-10}$$

$x << 0.100$, so
$0.100 - x \approx 0.100$

$$\frac{x^2}{0.100} = 5.89 \times 10^{-10}$$

$x = 7.6746496688 \times 10^{-6}$

$[OH^-] = x$, so

$pOH = 5.12$ ← (Need to convert OH- to hydronium. We'll use pOH to do this ...)

$pH = 14.00 - 5.12$

$pH = 8.88$

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

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

Check the ions formed in solution to see if they have acidic or basic properties.

Na^+: Not B-L acid, since there is no H+ to donate. Not likely to be B-L base due to the positive charge ... which would repel H+

Cl^-: Not B-L acid. Is is a B-L base? (It *is* negatively charged!)

$$Cl^- + H_2O \rightleftharpoons HCl + OH^-$$

HYDROCHLORIC ACID: This is a STRONG ACID. This means that HCl is not strable in water; it'll immediately lose any acquired protons! We conclude that chloride ion is NOT an effective B-L base.

Since neither sodium nor chloride ions affect pH, the pH of the solution is set by the water equilibrium. Therefore, the pH of the solution is 7.00 ... just like 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:

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

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

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, $pH = -\log(0.026267851)$

$$pH = 1.58$$

163 Find the pH of a solution prepared by dissolving 3.00 g of ammonium nitrate (FW=80.052 g/mol) solid into enough water to make 250. mL of solution.

What's the nature of ammonium nitrate? $NH_4NO_3 \rightarrow NH_4^+ + NO_3^-$

NO_3^- : $NO_3^- + H_2O \rightleftharpoons HNO_3 + OH^-$ <-- NITRIC ACID is a strong acid, so the nitrate ion should be NEUTRAL

NH_4^+ ; $NH_4^+ + H_2O \rightleftharpoons NH_3 + H_3O^+$ <-- AMMONIA is a weak base, so the ammonium ion should be ACIDIC!

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

$$K_a = \frac{[NH_3][H_3O^+]}{[NH_4^+]}$$

Ka value for ammonium ion? Page A-13 doesn't have it, but page A-14 has Kb for the conjugate. ammonia:

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

So $K_{a,NH_4^+} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$

To solve the equilibrium problem, we need to find the nominal concentration of our ammonium nitrate.

$80.052\ g\ NH_4NO_3 = mol\ NH_4NO_3$

$$3.00\ g\ NH_4NO_3 \times \frac{mol\ NH_4NO_3}{80.052\ g\ NH_4NO_3} = 0.037475640\ mol\ NH_4NO_3$$

$$[NH_4NO_3]_{nominal} = \frac{0.037475640\ mol\ NH_4NO_3}{0.250\ L} =$$

$$= 0.149902563\ M\ NH_4NO_3$$

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

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

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

Solve ...

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

$\downarrow$ $x \ll 0.14990$

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

$$x = 9.13 \times 10^{-6} = [H_3O^+]$$

$$pH = 5.04$$

... seems reasonable for a weakly acidic salt at moderate concentration.

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.

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

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

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

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

Assume x is small
$0.10 - x \approx 0.10$
$0.10 + x \approx 0.10$

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

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

So, pOH = 4.74

pH = 9.26

The common-ion effect suppresses the ionization of ammonia, raising the pH relative to the original ammonia solution (11.13)