$0.100\ M\ NaC_2H_3O_2$, Find pH

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

Check the ions formed by the salt to see if they're acidic, basic, or neutral:

Na^+: Not a B-L acid (no H+ to donate), and it's unlikely to be a B-L base due to the positive charge. This one is neutral.

$C_2H_3O_2^-$: Has H atoms, so could conceivably be B-L acid, but is more likely a B-L base due to the negative charge. Let's check:

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

This is ACETIC ACID ... a WEAK ACID. Since it's weak, it's stable in water and this reaction is possible.

$$\text{So, } K_b = \frac{[HC_2H_3O_2][OH^-]}{[C_2H_3O_2^-]} = ?$$

Kb for acetate ion isn't listed in our chart on page A-14, but on the previous page we can find the Ka for acetic acid.

$K_{a,\ HC_2H_3O_2} = 1.7 \times 10^{-5}$. Since $K_a \times K_b = 1.0 \times 10^{-14}$ for conjugates...

$$K_{b,\ C_2H_3O_2^-} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

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

Solve for the HYDROXIDE ION concentration , then convert to hydronium to get the answer to this problem.

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

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

$x << 0.100$

So, $0.100 - x \approx 0.100$

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

$$x^2 = 5.88 \times 10^{-11}$$

$$x = 7.67 \times 10^{-6} = [OH^-]$$

We need pH, but we have HYDROXIDE concentration ... don't forget to convert!

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

$$pOH = 5.12$$

$pH + pOH = 14.00$, so

$$pH = 14.00 - 5.12 = \boxed{8.86}$$

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 by the salt to see if they're acidic, basic, or neutral:

Na^+: Not a B-L acid (no H+ to donate), and it's unlikely to be a B-L base due to the positive charge. This one is neutral.

Cl^-: Not a B-L acid (no H+ to donate), but does have a negative charge and might attract H+. Is it a base?

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

This is hydrochloric acid ... a STRONG ACID. Since HCl is not stable in water (it's completely ionized), the chloride ion can't be called a base. It doesn't accept the proton, so it's neutral.

Since neither ion in sodium chloride affects pH, the pH is set by the water equilibrium alone, and the solution has a pH of 7.00 ... same as 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:

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

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

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!)

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

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

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

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

$$x = \frac{-0.0069 \pm 0.052986852}{2}$$

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

$$x = 0.0230 = [H_3O^+]$$

$$\boxed{pH = 1.64}$$

171 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.

Find out whether ammonium nitrate is acidic, basic, or neutral:

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

$$NH_4^+ : \quad NH_4^+ + H_2O \rightleftharpoons \boxed{NH_3} + H_3O^+$$

Ammonia is a weak base, stable in water. Ammonium is an ACID

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

Nitric acid is a STRONG ACID, so nitrate ion should be neutral.

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

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

$$\frac{K_{a,NH_4^+}}{K_{b,NH_3}} = 1.8\times10^{-5} \quad (p\,A\text{-}14)$$

$$\text{So, } K_a = \frac{1.0\times10^{-14}}{1.8\times10^{-5}} = 5.56\times10^{-10}$$

To set up the equilibrium here, we need to know the initial CONCENTRATIONS ... in MOLARITY units.

$$3.00\text{ g } NH_4NO_3 \text{ in } 0.250\text{ L}$$

$$3.00\text{ g } NH_4NO_3 \times \frac{\text{mol } NH_4NO_3}{80.052\text{ g } NH_4NO_3} = 0.0374756408\text{ mol } NH_4NO_3$$

$$[NH_4NO_3]_{\text{nominal}} = \frac{0.0374756408\text{ mol } NH_4NO_3}{0.250\text{ L}} = 0.149902563\text{ } \underline{M}$$

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

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

Species	[Initial]	Δ	[Equilibrium]
NH_3	0	$+x$	x
H_3O^+	0	$+x$	x
NH_4^+	0,149902S633	$-x$	0,149902S633 $- x$

Solve for x:

$$\frac{x^2}{0{,}149902S633 - x} = 5{,}56 \times 10^{-10}$$

$\downarrow$ $x \ll 0.150$, so $0.150 - x \approx 0.150$

$$\frac{x^2}{0{,}149902S633} = 5{,}56 \times 10^{-10}$$

$x^2 = 8.33 \times 10^{-11}$

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

$$\boxed{pH = 5.04}$$

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

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

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

Assume $x << 0.10$
$0.10 + x \simeq 0.10$
$0.10 - x \simeq 0.10$

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

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

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

$$\boxed{pH = 9.26}$$

The pH of the 0.10 M ammonia was 11.13, so we can conclude that the presence of ammonium ion SUPRESSES the ionization of ammonia. This demonstrates the COMMON-ION EFFECT.