

0.100 M  $\text{NaC}_2\text{H}_3\text{O}_2$ , Find pH



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

$\text{Na}^+$ : Not a B-L acid, since it has no  $\text{H}^+$  to donate. Not likely to be a B-L base either due to its positive charge. Sodium ion should be neutral (no effect on pH)

$\text{C}_2\text{H}_3\text{O}_2^-$ : Has H, so this could theoretically be B-L acid ... BUT it's more likely (with its negative charge) to be a B-L base.



This is ACETIC ACID ... a WEAK ACID. It's stable in water, so we expect acetate ion to function as a BASE.

$$\text{So, } K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = ?$$

$K_b$  for acetate ion isn't in our chart on page A-14, but on the previous page we can find the  $K_a$  for its conjugate - acetic acid.

$$\begin{array}{l|l} K_a, \text{HC}_2\text{H}_3\text{O}_2 = 1.7 \times 10^{-5} & \text{So, } K_b = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} \\ K_a \times K_b = 1.0 \times 10^{-14} & K_b = 5.88 \times 10^{-10} \end{array}$$

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



Species	[Initial]	$\Delta$	[Equil]
$HC_2H_3O_2$	0	+x	x
$OH^-$	0	+x	x
$C_2H_3O_2^-$	0.100	-x	0.100-x

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

$x \ll 0.100$   
 $0.100 - x \approx 0.100$

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

$$x = 7.67 \times 10^{-9} = [OH^-]$$

Remember ... we want pH, but this number is HYDROXIDE concentration.

$$pOH = -\log_{10}(7.67 \times 10^{-9})$$

$$pOH = 5.12$$

$$pH = 14 - 5.12 = \boxed{8.88}$$

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



Check the ions formed by the salt:

$\text{Na}^+$ : Not a B-L acid, since it has no  $\text{H}^+$  to donate. Not likely to be a B-L base either due to its positive charge. Sodium ion should be neutral (no effect on pH)

$\text{Cl}^-$ : Not a B-L acid, but might be a B-L base due to its negative charge.



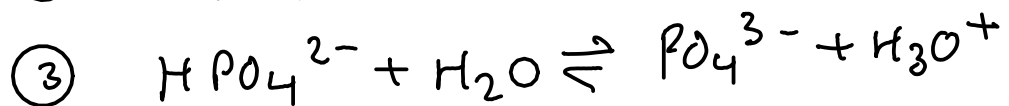
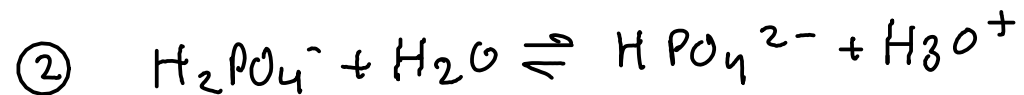
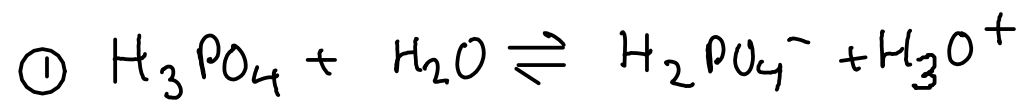
This is hydrochloric acid ... a STRONG ACID. It completely ionizes in water (it's unstable), so that means that chloride ion is NOT able to act as a B-L base in water!

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Since neither ion has acidic or basic properties, the pH is set by the water equilibrium, and the solution has a pH of 7.00

Find pH of 0.10 M  $\text{H}_3\text{PO}_4$

... what's special about phosphoric acid?



Phosphoric acid has THREE acidic protons!

$$K_{a1} = 6.9 \times 10^{-3}$$

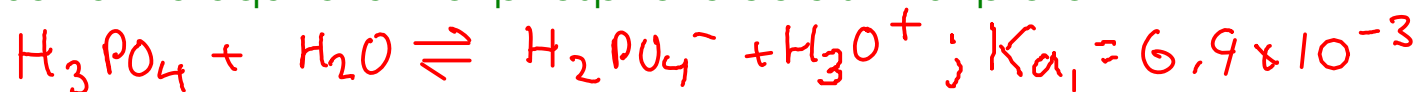
$$K_{a2} = 6.2 \times 10^{-8}$$

$$K_{a3} = 4.8 \times 10^{-13}$$

The first dissociation 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:



$$K_a = \frac{[\text{H}_2\text{PO}_4^-][\text{H}_3\text{O}^+]}{[\text{H}_3\text{PO}_4]} = 6.9 \times 10^{-3}$$

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{H}_3\text{PO}_4$	0.10	-x	0.10 - x
$\text{H}_2\text{PO}_4^-$	0	+x	x
$\text{H}_3\text{O}^+$	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  $x \ll 0.10$  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!)

$$x = 0.0230 = [\text{H}_3\text{O}^+]$$

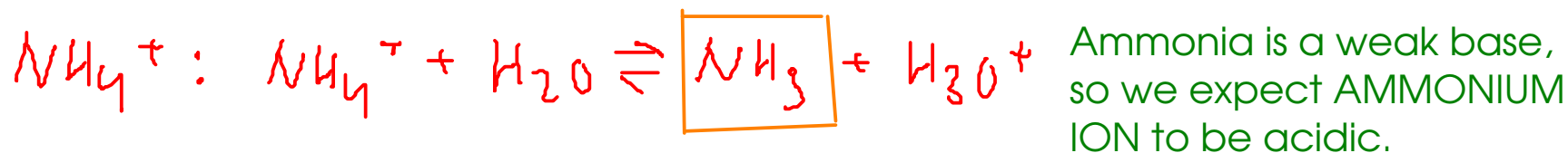
$$\text{pH} = 1.64$$

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 the nature of the salt ... acid, base, neutral?



Nitric acid is strong (unstable), so NITRATE should be NEUTRAL



Ammonia is a weak base, so we expect AMMONIUM ION to be acidic.



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

To set up the equilibrium, we need molar concentration of the ammonium ion:

3.00 g  $\text{NH}_4\text{NO}_3$  in 250. mL, or 0.250 L solution

$$3.00 \text{ g } \text{NH}_4\text{NO}_3 \times \frac{\text{mol } \text{NH}_4\text{NO}_3}{80.052 \text{ g } \text{NH}_4\text{NO}_3} = 0.0374756408 \text{ mol } \text{NH}_4\text{NO}_3$$

$$[\text{NH}_4^+]_{\text{initial}} = \frac{0.0374756408 \text{ mol } \text{NH}_4\text{NO}_3}{0.250 \text{ L}} = 0.14990 \text{ M}$$

$$K_a, \text{NH}_4^+ : (K_a \times K_b = 1.0 \times 10^{-14})$$

$$K_b, \text{NH}_3 = 1.8 \times 10^{-5}$$

$$\text{So } K_a, \text{NH}_4^+ = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-5}}$$

$$K_a = 5.56 \times 10^{-10}$$



$$K_a = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = 5.56 \times 10^{-10}$$

Species	[Initial]	$\Delta$	[Equil]
$\text{NH}_3$	0	+x	x
$\text{H}_3\text{O}^+$	0	+x	x
$\text{NH}_4^+$	0.14990	-x	0.14990 - x

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

$x \ll 0.14990$   
 $0.14990 - x \approx 0.14990$

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

$$x = 9.13 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5.04$$

This pH seems reasonable for a weakly 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 Chateleur's Principle applied to equilibria involving ions



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?



The ammonium chloride provides the ammonium ion. According to Le Chateleur'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 contains 0.10 M ammonia AND 0.10 M ammonium chloride.



Species	[Init]	$\Delta$	[Equil]
$\text{NH}_4^+$	0.10	+x	0.10+x
$\text{OH}^-$	0	+x	x
$\text{NH}_3$	0.10	-x	0.10-x

$$\frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]} = 1.8 \times 10^{-5}$$

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

Assume  $x \ll 0.10$

$$0.10 - x \approx 0.10$$

$$0.10 + x \approx 0.10$$

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

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

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

$$\text{pH} = 9.26$$

The common-ion effect suppresses the ionization of the ammonia, resulting in a lower pH relative to the 0.10 M ammonia solution.

## BUFFERS

- resist pH change caused by either the addition of strong acid/base OR by dilution

Made in one of two ways:

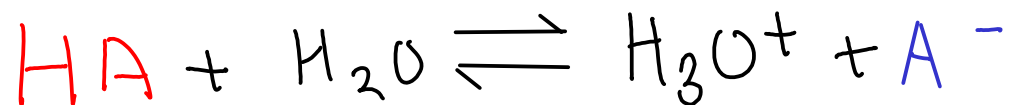
- ① Make a mixture of a weak acid and its conjugate base (as the SALT)  
 $\text{HC}_2\text{H}_3\text{O}_2$                        $\text{NaC}_2\text{H}_3\text{O}_2$
- ② Make a mixture of a weak base and its conjugate acid (as the SALT)  
 $\text{NH}_3$                                        $\text{NH}_4\text{Cl}$

For a weak acid, you would:



- Add HA (weak acid)
- Add a salt containing  $\text{A}^-$  (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.



$$K_a = \frac{[H_3O^+][A^-]}{[HA]}$$

① Take log of both sides

② Multiply by -1

③ Rearrange, solving for pH

$$pH = pK_a + \log\left(\frac{[A^-]}{[HA]}\right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

$[A^-]$  ... 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.