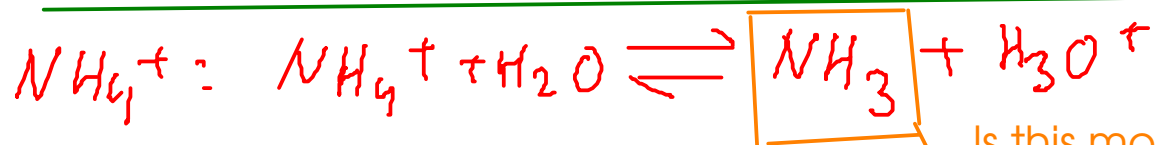
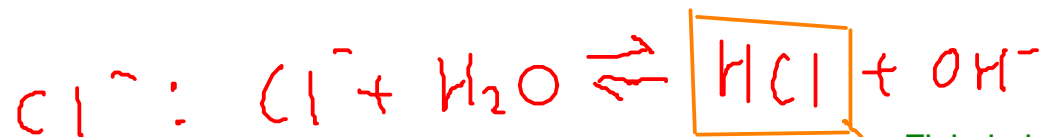


0.100 M  $\text{NH}_4\text{Cl}$  ... Find the pH of the solution

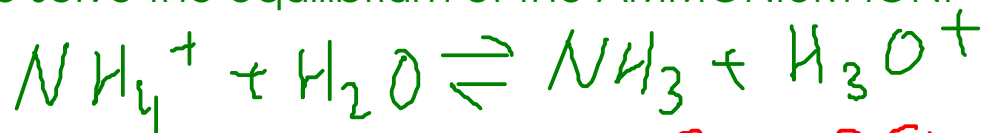


Is this molecule stable in water? YES.  
Ammonia is a common weak base that can exist in water.



This is hydrochloric acid ... a STRONG ACID.  
HCl completely ionizes in water, meaning that HCl is NOT stable in water. Therefore,  $\text{Cl}^-$  is NEUTRAL.

So, we solve the equilibrium of the AMMONIUM ION:



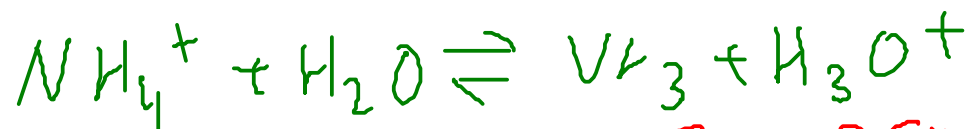
$$K_{a, \text{NH}_4^+} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]} = ?$$

On pages A-13, there's no  $K_a$  for ammonium ion ... but there IS a  $K_b$  on A-14 for ammonia:

$$K_{b, \text{NH}_3} = 1.8 \times 10^{-5} \quad ; \quad (K_{a, \text{NH}_4^+})(K_{b, \text{NH}_3}) = 1.0 \times 10^{-14}$$

$$(K_{a, \text{NH}_4^+})(1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$$

$$K_{a, \text{NH}_4^+} = 5.56 \times 10^{-10}$$



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

Now solve this equilibrium just like you would for any weak acid ...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{NH}_3$	0	+x	x
$\text{H}_3\text{O}^+$	0	+x	x
$\text{NH}_4^+$	0.100	-x	0.100 - x

$$\frac{(x)(x)}{0.100 - x} = 5.56 \times 10^{-10}$$

$$\frac{x^2}{0.100 - x} = 5.56 \times 10^{-10}$$

$$\downarrow x \ll 0.100$$

$$\frac{x^2}{0.100} = 5.56 \times 10^{-10}$$

$$x^2 = 5.56 \times 10^{-11}$$

$$x = 7.45 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\boxed{\text{pH} = 5.13}$$

Compare:

pH = 1.00 for 0.10 M strong acid

pH = 2.17 for 0.10 M nitrous acid (weak acid)

pH = 7.00 for distilled water.

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 (no  $\text{H}^+$  to donate), and it's unlikely to be a B-L base due to the positive charge. This one is neutral.

$\text{C}_2\text{H}_3\text{O}_2^-$ : 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:



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

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

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

$K_a, \text{HC}_2\text{H}_3\text{O}_2 = 1.7 \times 10^{-5}$ . Since  $K_a \times K_b = 1.0 \times 10^{-14}$  for conjugates...

$$K_b, \text{C}_2\text{H}_3\text{O}_2^- = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}} = 5.88 \times 10^{-10}$$

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} = 5.88 \times 10^{-10}$$

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

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{HC}_2\text{H}_3\text{O}_2$	0	+X	X
$\text{OH}^-$	0	+X	X
$\text{C}_2\text{H}_3\text{O}_2^-$	0.100	-X	0.100 - X

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

$x \ll 0.100$   
 $\downarrow$  So,  $0.100 - x \approx 0.100$

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

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

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

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

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

$$\text{pOH} = 5.12$$

$$\text{pH} + \text{pOH} = 14.00, \text{ so}$$

$$\text{pH} = 14.00 - 5.12 = \boxed{8.88}$$

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!

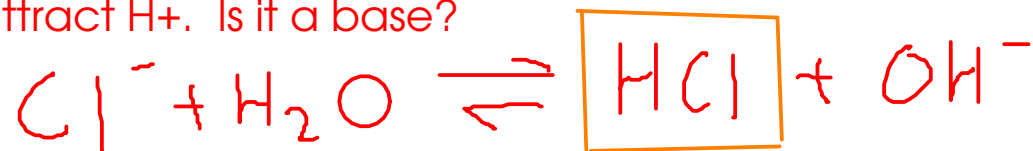
0.100 M NaCl, Find pH



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

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

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

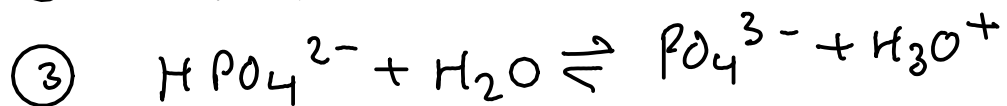
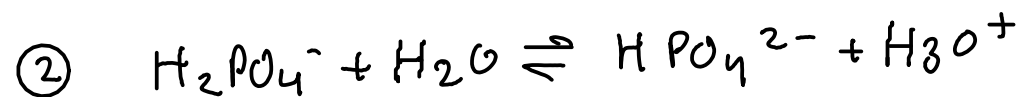
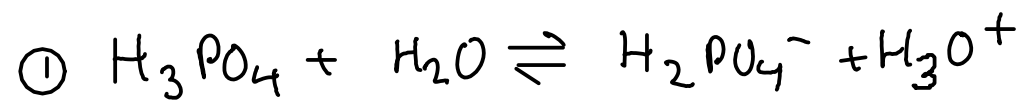


This is hydrochloric acid ... a STRONG ACID. Since HCl is not stable in water (it's completely ionized), the chloride ion can't be called a base. It doesn't accept the proton, so it's neutral.

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.

Find pH of 0,10 M  $\text{H}_3\text{PO}_4$

... what's special about phosphoric acid?



Phosphoric acid has **THREE** acidic protons!

$$K_{a1} = 6,9 \times 10^{-3}$$

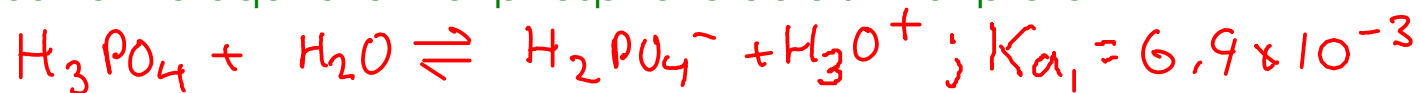
$$K_{a2} = 6,2 \times 10^{-8}$$

$$K_{a3} = 4,8 \times 10^{-13}$$

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!)

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

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

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

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

$$x = \frac{-0.0069 \pm 0.0529868852}{2}$$

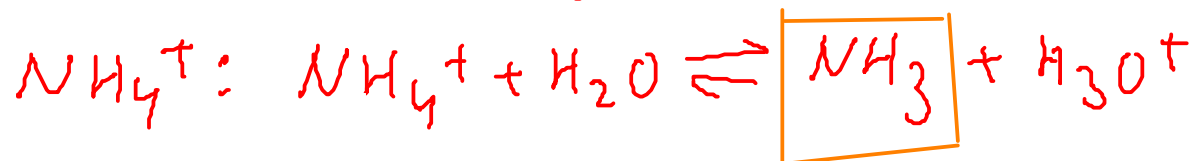
Discard the negative root. 'x' can't be less than zero (it's equal to two of the concentrations!)

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

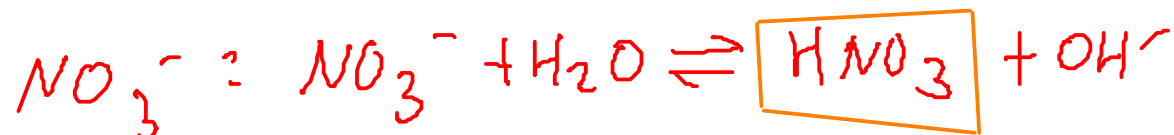
$$\text{pH} = 1.64$$



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.



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



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



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

$$K_{a, \text{NH}_4^+}$$

$$K_{b, \text{NH}_3} = 1.8 \times 10^{-5} \quad (pK_b = 14)$$

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

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

3.00 g  $\text{NH}_4\text{NO}_3$  in 0.250 L

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

$$[\text{NH}_4\text{NO}_3]_{\text{nominal}} = \frac{0.0374756408 \text{ mol } \text{NH}_4\text{NO}_3}{0.250 \text{ L}} = 0.1499025633 \text{ M}$$



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

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{NH}_3$	0	+x	x
$\text{H}_3\text{O}^+$	0	+x	x
$\text{NH}_4^+$	0,1499025633	-x	0,1499025633 - x

Solve for x:

$$\frac{x^2}{0,1499025633 - x} = 5,56 \times 10^{-10}$$

$\downarrow$   $x \ll 0,150$ , so  $0,150 - x \approx 0,150$

$$\frac{x^2}{0,1499025633} = 5,56 \times 10^{-10}$$

$$x^2 = 8,33 \times 10^{-11}$$

$$x = 9,13 \times 10^{-6} = [\text{H}_3\text{O}^+]$$

$$\text{pH} = 5,04$$

## 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 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 .

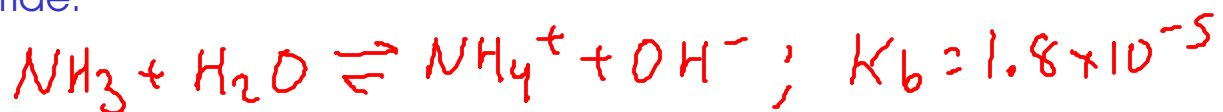
What would happen to the pH if we dissolved ammonium chloride into the solution?



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	[Initial]	$\Delta$	[Equilibrium]
$\text{NH}_4^+$	0.10	+x	0.10+x
$\text{OH}^-$	0	+x	x
$\text{NH}_3$	0.10	-x	0.10-x

$$K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$$

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

Assume  $x \ll 0.10$   
 $0.10 - x \approx 0.10$   
 $0.10 + x \approx 0.10$

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

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

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

$$\text{pOH} = 4.74$$

$$\text{pH} = 9.26$$

The common-ion effect suppresses the ionization of ammonia, lowering the pH compared to the ammonia solution's pH of 11.13 ...

## 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.