

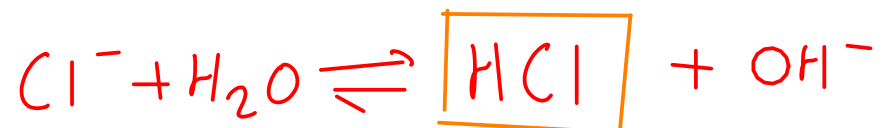
0.100 M NaCl, Find pH



To find out if NaCl is acidic, basic, or neutral ... look at the ions.

$\text{Na}^+$  : Not a B-L acid (no  $\text{H}^+$  to donate), Not a B-L base (not likely to attract  $\text{H}^+$  due to positive charge). Neutral.

$\text{Cl}^-$  : Not a B-L acid (no  $\text{H}^+$  to donate). How about a base? Let's check.



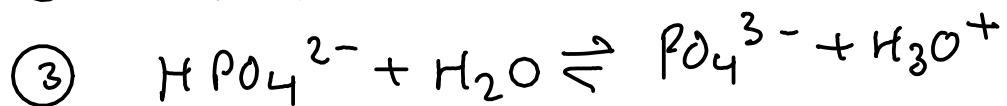
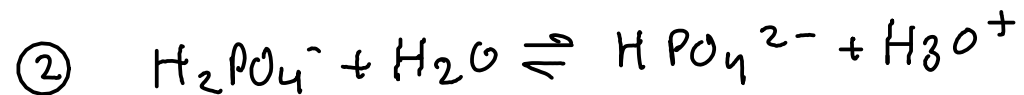
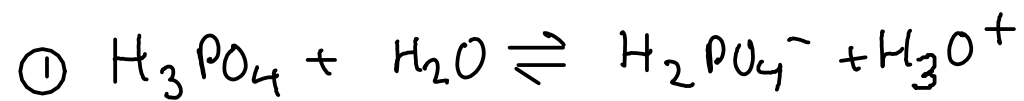
HCl (hydrochloric acid) is a STRONG ACID. This means that chloride ion can't hold onto a  $\text{H}^+$  and is therefore NOT a base.

Chloride ion is also neutral.

The pH of the solution is 7.00, since the water equilibrium itself is setting the pH.

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

... what's special about phosphoric acid?



Phosphoric acid has THREE acidic protons!

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

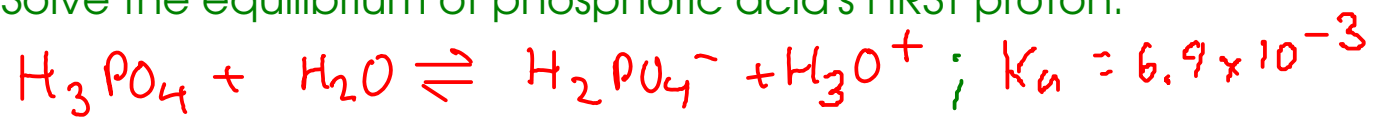
$$K_{a2} = 6.2 \times 10^{-8}$$

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

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]
$\text{H}_2\text{PO}_4^-$	0	+x	x
$\text{H}_3\text{O}^+$	0	+x	x
$\text{H}_3\text{PO}_4$	0.10	-x	0.10 - x

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

assume  $x \ll 0.10$   
so  $0.10 - x \approx 0.10$

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

$$x = 0.0262678511 = [\text{H}_3\text{O}^+]$$

$$\text{So, } \text{pH} = -\log(0.0262678511)$$

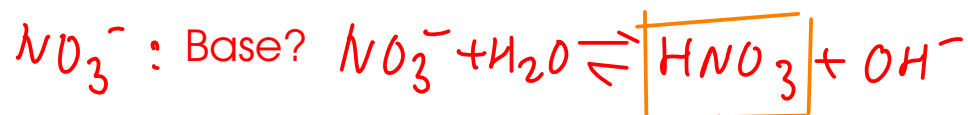
$$\text{pH} = 1.58$$

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.

Find out whether this salt is acidic or basic?  $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^-$



Since AMMONIA is a WEAK BASE, it's stable in water. Ammonium, then, should be able to act as an acid.



STRONG ACID (like HCl), so nitrate ion won't act as a base.

The pH will be set by the equilibrium of AMMONIUM ION (an ACID equilibrium)

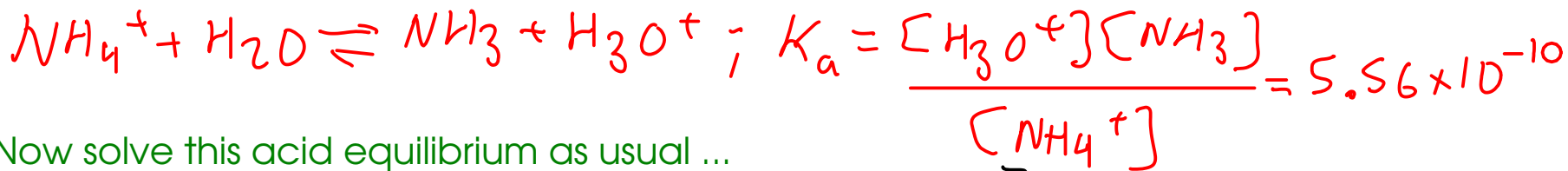


We need a value for  $K_a$ . Consult chart on p A-13 to A-14. We don't find a  $K_a$  for AMMONIUM ION, but we \*do\* find a  $K_b$  for AMMONIA (the conjugate of ammonium ion). We can make use of this since for any conjugate pair,  $K_a \cdot K_b = K_w$  ...

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

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

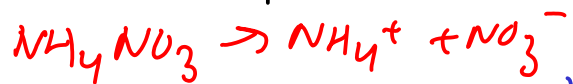
$$K_{a, \text{NH}_4^+} = 5.56 \times 10^{-10}$$



Now solve this acid equilibrium as usual ...

Species	[Initial]	$\Delta$	[Equilibrium]
$\text{H}_3\text{O}^+$	0	+ X	X
$\text{NH}_3$	0	+ X	X
$\text{NH}_4^+$	0.1499025633	- X	0.1499025633 - X

Let "x" equal the change in hydronium ion concentration.



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

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

Plug into expression for  $K_a$  ...

$$\frac{(x)(x)}{0.1499025633 - x} = 5.56 \times 10^{-10}$$

$$\downarrow x \ll 0.1499$$

$$\frac{x^2}{0.1499025633} = 5.56 \times 10^{-10}$$

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

$$\text{pH} = 5.04$$

## 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.



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

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

Let "x" equal the change in ammonium ion concentration.

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

Assume x is small compared to 0.10, so  
 $0.10 - x = 0.10$ , and  $0.10 + x = 0.10$

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

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

$$\text{pOH} = 4.74$$

$$\text{pH} = 14.00 - 4.74$$

$$\boxed{\text{pH} = 9.26}$$

(The pH of the 0.10 M ammonia-only solution was 11.13...)

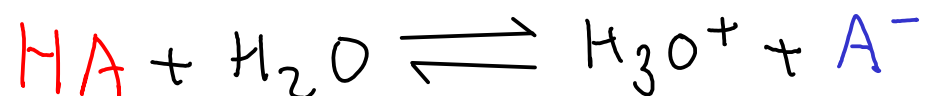
## BUFFERS

- 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)  
 $\text{NH}_3$                                        $\text{NH}_4\text{Cl}$

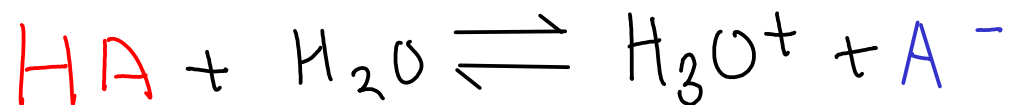
For a weak acid, you would:



- 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.





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

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.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

ex: acidic buffer



$$\text{pH} = \text{p}K_{a, \text{HC}_2\text{H}_3\text{O}_2} + \log \left( \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \right)$$

ex: basic buffer



$$\text{pH} = \text{p}K_{a, \text{NH}_4^+} + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]} \right)$$

$$\text{p}K_a + \text{p}K_b = 14,00 \quad \dots \text{ is the } -\log \text{ of } K_a \times K_b = K_w$$

Calculate the pH of a buffer made from 30.2 grams of ammonium chloride (FW = 53.492 g/mol) and 29 mL of 18.1 M ammonia diluted to 150. mL with water.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right) \quad \left| \begin{array}{l} \text{Henderson-} \\ \text{Hasselbalch} \\ \text{Equation} \end{array} \right.$$

First, calculate concentrations of ammonium and ammonia.

$$[\text{NH}_3]: m_1 V_1 = m_2 V_2 \quad (29 \text{ mL})(18.1 \text{ M}) = M_2 (150. \text{ mL})$$

$$M_2 = 3.499333333 \text{ M NH}_3$$

$$[\text{NH}_4^+]: 30.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}} = 0.5645704031 \text{ mol NH}_4\text{Cl}$$

$$\text{since mol NH}_4\text{Cl} = \text{mol NH}_4^+$$

$$\frac{0.5645704031 \text{ mol NH}_4^+}{0.150 \text{ L}} = 3.763802687 \text{ M NH}_4^+$$

$$\text{pH} = \text{p}K_{a, \text{NH}_4^+} + \log \left( \frac{[\text{NH}_3]}{[\text{NH}_4^+]}\right)$$

$$= 9.26 + \log \left( \frac{3.499333333}{3.763802687} \right)$$

$$= \boxed{9.22}$$

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

$$K_a \times K_b = 1.0 \times 10^{-14}, \text{ so}$$

$$K_a (1.8 \times 10^{-5}) = 1.0 \times 10^{-14}$$

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

$$\text{p}K_a = 9.26$$

## <sup>171</sup> BUFFER SELECTION

- Buffer pH is controlled by the pKa of the acidic species in the buffer.

$$\text{pH} = \text{p}K_{a, \text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right)$$

- Choose a buffer system so that the desired pH is within +/- 1 pH unit of the pKa
- You also need to ensure that the components of the buffer do not interact with your chemistry!

## BUFFER PREPARATION

- many buffers are prepared by mixing specific amounts of both components of the Buffer system (acid / conjugate base or base / conjugate acid)

Some buffer "recipes" call for making the conjugate ion FROM the weak acid or base ... by adding a STRONG acid or base!



The reaction of the strong acid with the weak base goes essentially to completion!

If you have more ammonia than nitric acid, you will end up with a solution containing a significant amount of both ammonia and ammonium ion ... a buffer!

## BUFFER CAPACITY

- A buffer is good only as long as there is a significant concentration of both the acidic and basic species
- buffer capacity: how much acid or base can a buffer resist before losing its ability to buffer
- Buffer pH depends on the RATIO of acid to base!

$$\text{pH} = \text{p}K_{a,\text{acidic}} + \log \left( \frac{[\text{basic species}]}{[\text{acidic species}]} \right)$$

Henderson-Hasselbalch Equation

Ratio determines pH; the actual concentrations don't!

- So, if you make a buffer with 1.0M HA and 1.0M A<sup>-</sup>, it will have the same pH as a buffer with 2.0M HA and 2.0M A<sup>-</sup> .... but the 2M buffer will have a higher BUFFER CAPACITY - it will resist more additions of acid or base.