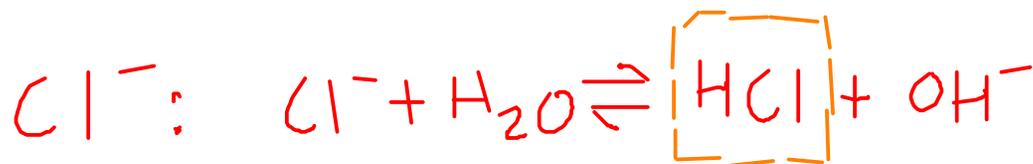


0.100 M NaCl, Find pH



Check the ions produced by sodium chloride for acidic or basic properties ...

$\text{Na}^+$ . Cannot be B-L acid (no  $\text{H}^+$  to donate), and unlikely to be B-L base due to the charge. Likely NEUTRAL.

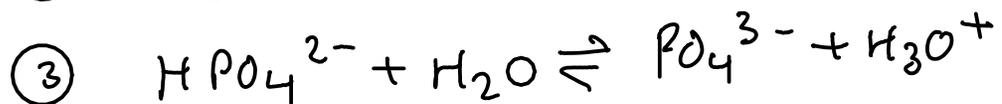
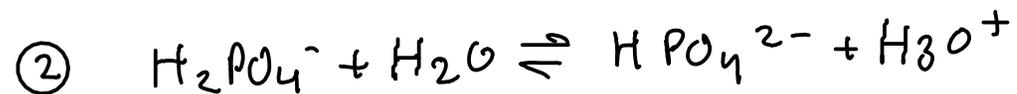
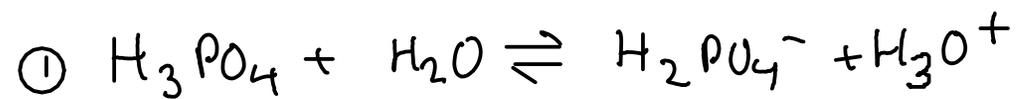


HCl is a STRONG acid, meaning that it's not stable in water. So,  $\text{Cl}^-$  ion will not be able to accept a proton from water. It's NEUTRAL.

Neither  $\text{Na}^+$  nor  $\text{Cl}^-$  are acidic or basic. So what controls the pH in this solution? The water equilibrium itself. Therefore, the pH is 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!

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

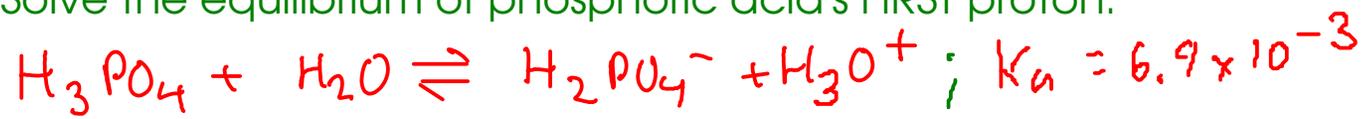
$$K_{a2} = 6.2 \times 10^{-8}$$

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

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]
$\text{H}_2\text{PO}_4^-$	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  $0.10 - x \approx 0.10$

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

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

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

$$\text{pH} = 1.58$$

## 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 .

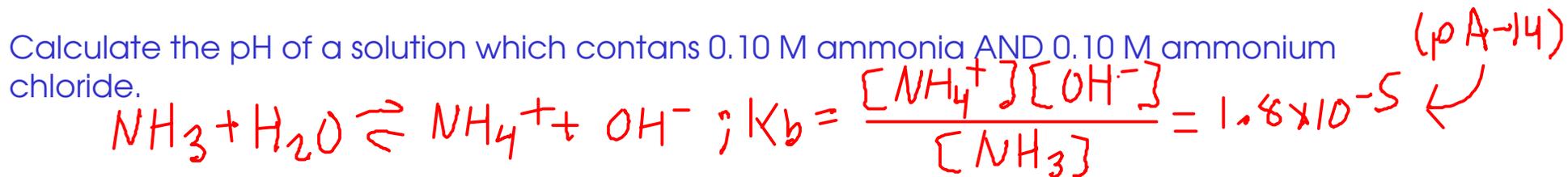
What would happen to the pH if we dissolved ammonium chloride into the solution?



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

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

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

Assume  $x \ll 0.10$ , so ...

$\downarrow$   $0.10-x \approx 0.10$  and  $0.10+x \approx 0.10$

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

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

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

$$\text{pOH} = 4.74$$

$$\text{pH} = 9.26$$

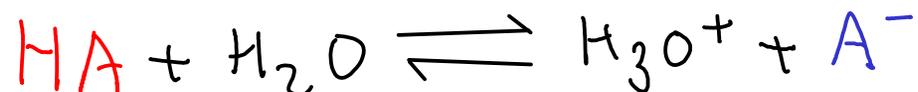
## BUFFERS

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

Made in one of two ways:

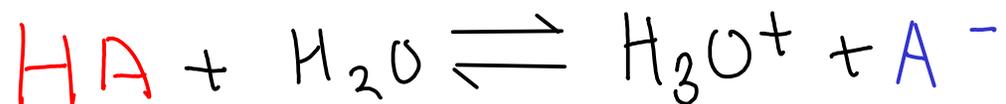
- ① Make a mixture of a weak acid and its conjugate base (as the SALT)  
 $\text{HC}_2\text{H}_3\text{O}_2$                        $\text{NaC}_2\text{H}_3\text{O}_2$
- ② Make a mixture of a weak base and its conjugate acid (as the SALT)  
 $\text{NH}_3$                                        $\text{NH}_4\text{Cl}$

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.

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

$$\text{NH}_3: m_1v_1 = m_2v_2 \quad (18.1\text{ M})(29\text{ mL}) = M_2(150\text{ mL}) \quad \text{Find base concentration}$$

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

$$\text{NH}_4^+: 30.2\text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492\text{ g NH}_4\text{Cl}} = 0.5645704031\text{ mol NH}_4^+ \quad \text{Find acid concentration}$$

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

$$K_{a,\text{NH}_4^+} = ? \quad K_{b,\text{NH}_3} = 1.8 \times 10^{-5}; \quad \text{p}K_b = 4.74, \quad \text{p}K_a = 14 - \text{p}K_b = 9.26$$

(We need pKa for the Henderson-Hasselbalch equation!) (pKa + pKb = 14.00)

$$\text{pH} = 9.26 + \log\left(\frac{3.499333333\text{ M NH}_3}{3.763802687\text{ M NH}_4^+}\right) = \boxed{9.23}$$