

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?

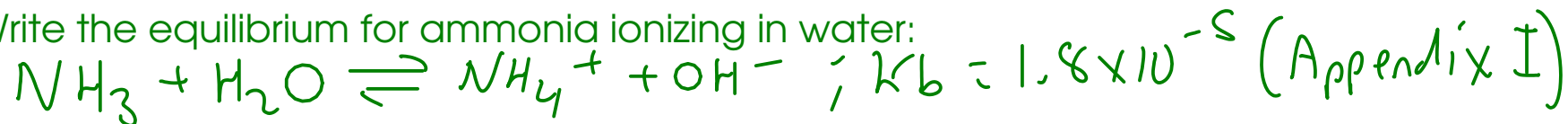


The ammonium chloride provides the ammonium ion. According to Le Chateleur's principle, this would shift the ammonia equilibrium to the LEFT!

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.

Write the equilibrium for ammonia ionizing in water:



Solve the equilibrium as normal:

Species	[Initial]	Δ	[Equilibrium]
NH_3	0.10	-x	0.10 - x
NH_4^+	0.10	+x	0.10 + x
OH^-	0	+x	x

Let "x" equal the change in ammonia concentration

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

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

$x \ll 0.10$
 \downarrow
 $0.10 - x \approx 0.10$
 $0.10 + x \approx 0.10$
 $\frac{0.10x}{0.10} = 1.8 \times 10^{-5}$

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

$$\text{pOH} = 4.74$$

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

$$\text{pOH} = -\log_{10} [\text{OH}^-]$$

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

(The pH of the 0.10 M ammonia 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:

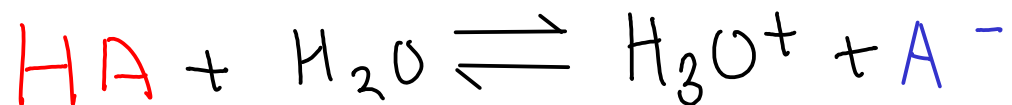
- ① Make a mixture of a weak acid and its conjugate base (as the SALT)
 $\text{HC}_2\text{H}_3\text{O}_2$ $\text{NaC}_2\text{H}_3\text{O}_2$
- ② Make a mixture of a weak base and its conjugate acid (as the SALT)
 NH_3 NH_4Cl

For a weak acid, you would:



- Add HA (weak acid)
- Add a salt containing 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.

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

$$3.50 \text{ M NH}_3 = M_2$$

$$[\text{NH}_4^+]: \quad 30.2 \text{ g NH}_4\text{Cl} \times \frac{\text{mol NH}_4\text{Cl}}{53.492 \text{ g NH}_4\text{Cl}} = 0.56457 \text{ mol NH}_4\text{Cl}$$

$$\frac{0.56457 \text{ mol NH}_4\text{Cl}}{0.150 \text{ L}} = 3.76 \text{ M NH}_4\text{Cl} = 3.76 \text{ M NH}_4^+$$

$$\text{p}K_{a, \text{NH}_4^+} = ? \quad K_{b, \text{NH}_3} = 1.8 \times 10^{-5} \text{ (Appendix I)}, \text{p}K_b = 4.74 \quad \text{p}K_b = -\log_{10} K_b$$

$$\text{so, p}K_a = 9.26 \quad \text{p}K_a + \text{p}K_b = 14.00$$

$$\text{pH} = 9.26 + \log \left(\frac{3.50}{3.76} \right) = \boxed{9.23}$$

¹⁵¹ 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!