${ }^{163}$ 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.
First, let's determine what kind of salt we have - acidic, basic, or neutral:
$\mathrm{NH}_{4} \mathrm{NO}_{3} \rightarrow \mathrm{NH}_{4}{ }^{+}+\mathrm{NO}_{3}$ - Is either of these two ions acidic or basic?
$\mathrm{NL}_{2}++\mathrm{H}_{2} \mathrm{O} \rightleftarrows \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+} \begin{aligned} & \text { Ammonia (NH3) is a WEAK base, meaning it's } \\ & \text { stable in water and ammonium ion should be }\end{aligned}$ ACIDIC!

$$
\mathrm{NO}_{3}^{-}+\mathrm{H}_{2} \mathrm{O} \underset{\mathrm{~F}}{\mathrm{~F}} \mathrm{HO}_{3}+\mathrm{OH}_{4}-\begin{aligned}
& \text { NITRIC ACID is a STRONG acid, therefore nitrate ion } \\
& \text { cant hang onto the proton and is NEUTRAL. }
\end{aligned}
$$

$$
\begin{aligned}
& \quad \mathrm{NH}_{4}^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{K}_{a}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3 \mathrm{O}^{+}}\right]}{\left[\mathrm{NH}_{4}^{+}\right]} \\
& \text {We need to solve ammonium ion's equilibrium. } \\
& \text { First, find Ka (you'll need to get it from the Kb of the conjugate ---->) }
\end{aligned}
$$

We need to set up an equilibrium chart, but those concentrations are in molarity units. So let's get the initial ammonium nitrate concentration in molarity units!

$$
\begin{aligned}
& 3.00 \mathrm{gNH} 4_{4} \mathrm{NO}_{3} \times \frac{\mathrm{mol} \mathrm{NH}}{4} \mathrm{NO}_{3} \\
& 80.052 \mathrm{gH}_{4} \mathrm{NO}
\end{aligned}=0.0374756400 \mathrm{~mol}_{3} \mathrm{NH}_{4} \mathrm{NO}_{3}
$$

164

$$
\begin{aligned}
& \mathrm{NH}_{4}{ }^{+}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{NH}_{3}+\mathrm{H}_{3} \mathrm{O}^{+}, \mathrm{K}_{4}=\frac{\left[\mathrm{NH}_{3}\right]\left[\mathrm{H}_{3} \mathrm{O}^{+}\right]}{\left[\mathrm{NH}_{4}^{+}\right]}=5.56 \times 10^{-10} \\
& 0.1499025633 \mathrm{mNH}_{4}^{-} \text {<-- concentration of acid }
\end{aligned}
$$

Set up equilibrium chart and solve!

| Species | [Initial] | $A$ | $\left[E_{\text {quilibrivm }}\right.$ ] |
| :---: | :---: | :---: | :---: |
| $\mathrm{H}_{30^{+}}$ | 0 | $+X$ | $X$ |
| $\mathrm{NH}_{3}$ | 0 | $+X$ | $X$ |
| $\mathrm{NH}_{4}+$ | 0.1499025633 m | $-X$ | $0.1499025633-\mathrm{X}$ |

Let "x" equal the change in hydronium ion concentration

$$
\begin{aligned}
& \frac{(x)(x)}{(0.1494025633-x)}=5.56 \times 10^{-10} \\
& \frac{x^{2}}{0.1499025633-x}=5.56 \times 10^{-10}
\end{aligned}
$$

$$
x=9.129393475 \times 10^{-6} \mathrm{~m} \mathrm{H}_{3} \mathrm{O}^{+}
$$

$$
p H=5.04 \quad\left(p H=-\log _{10}\left[H_{3} 0^{+}\right]\right)
$$

- is the effect on the ionization of a compound caused by the presence of an ion involved in the equilibrium
- is essentially Le Chateleir's Principle applied to equilibria involving ions
ex: $\mathrm{NH}_{3}(\mathrm{aq})+\mathrm{H}_{2} \mathrm{O}(l) \rightleftharpoons \mathrm{NH}_{4}{ }^{t}\left(\mathrm{aq}_{q}\right)+\mathrm{OH}^{-}(\mathrm{aq}) ; \mathrm{K}_{b}=1.8 \times 10^{-5}$
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?
$\mathrm{NH}_{4} \mathrm{Cl}(\mathrm{s}) \rightarrow \mathrm{NH}_{q}{ }^{+}(\mathrm{aq})+\mathrm{Cl}^{-}(\mathrm{aq})$
The ammonium chloride provides the ammonium ion. According to Le Chateleir'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 contans 0.10 M ammonia AND 0.10 M ammonium chloride.

$$
\begin{aligned}
& \mathrm{NH}_{4} \mathrm{Cl} \rightarrow \mathrm{NH}_{4}{ }^{+}+\mathrm{Cl}^{-} \text {(The salt makes ammonium ion) } \\
& \mathrm{NH}_{4}{ }^{+}+\mathrm{OH}^{-} ; \mathrm{K}_{6}=\frac{\left[\mathrm{NH}_{4}+\right]\left[\mathrm{OH}^{-}\right]}{\left[\mathrm{NH}_{3}\right]}=1.8 \times 10^{-\mathrm{S}}(\mathrm{\rho A}-14)
\end{aligned}
$$

Set up and solve the ammonia equilibrium...

| Species | [Initial] | $A$ | CEqillibrium $]$ |
| :--- | :---: | :---: | :---: |
| $\mathrm{OH}^{-}$ | 0 | $+x$ | $x$ |
| $\mathrm{NH}_{4}^{+}$ | 0.10 | $+x$ | $0.10+x$ |
| $\mathrm{NH}_{3}$ | 0.10 | $-x$ | $0.10-x$ |

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

$$
\begin{gathered}
\frac{(0.10+y)(x)}{(0.10-x)}=1.8 \times 10^{-5} \\
\begin{array}{c}
\text { Assume } x<00.10 \\
0.10-x \approx 0,10 \\
0.10+y=0,10 \\
\frac{0.10 x}{0.10}=1.8 \times 10^{-5}
\end{array}
\end{gathered}
$$

$$
x=1,8 \times 10^{-5} \mathrm{~m} \mathrm{oH}
$$

## BUFFERS

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

Made in one of two ways:

$$
\mathrm{HC}_{2} \mathrm{H}_{3} \mathrm{O}_{2} \quad \mathrm{NaC}_{2} \mathrm{H}_{3} \mathrm{O}_{2}
$$

(1)Make a mixture of a weak acid and its conjugate base (as the SALT)
(2) Make a mixture of a weak $\mathrm{NH}_{3}$ ase and its conjugate acid (as the SALT)

For a weak acid, you would:

$$
\begin{aligned}
H A+ & H_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-} \\
& \text {- Add HA (weak acid) } \\
& \text { - Add a salt containing } A^{-} \text {(example: } \mathrm{NaA} \text { ) }
\end{aligned}
$$

- 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.

$$
\begin{gathered}
\mathrm{HA}+\mathrm{H}_{2} \mathrm{O} \rightleftharpoons \mathrm{H}_{3} \mathrm{O}^{+}+\mathrm{A}^{-} \\
k_{a}=\frac{\left[\mathrm{H}_{3} \mathrm{O}^{+}\right][\mathrm{A}]}{[\mathrm{HA}]}
\end{gathered}
$$

(1) Take log of both sides
(2) Multiply by -1
(3) Rearrange, solving for pH

$$
p H=p K_{a}+\log \left(\frac{\left[A^{-}\right]}{[H A]}\right) \left\lvert\, \begin{aligned}
& \text { Henderson- } \\
& \begin{array}{l}
\text { Hasselbalch } \\
\text { Equation }
\end{array}
\end{aligned}\right.
$$

$[A-] \ldots$ from the salt $[\mathrm{HA}] \ldots$ 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.

