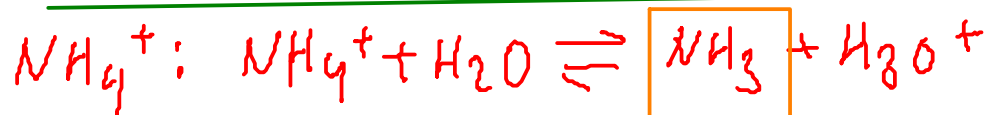
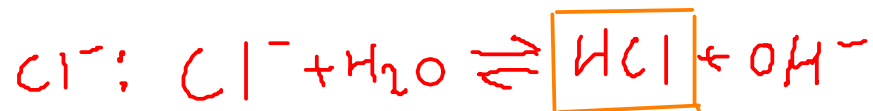


0.100 M NH_4Cl ... Find the pH of the solution

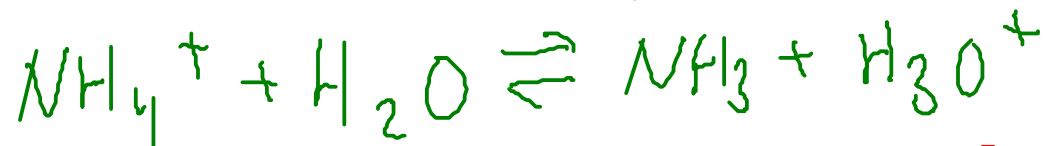


Is this molecule stable in water? YES ...
Ammonia is a weak base (meaning it exists mostly as molecules when dissolved in water!)

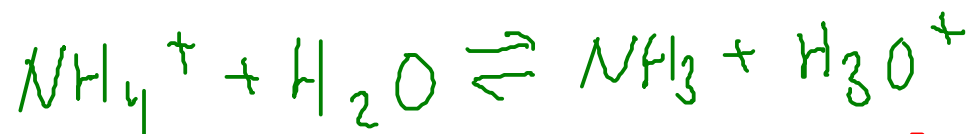


HCl is a STRONG ACID ... in other words, it ionizes completely in water. Therefore, Cl^- is not going to be a proton acceptor. It's NEUTRAL.

So, we will need to solve this equilibrium:



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



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

Once we've calculated K_a ... this problem is solvable the same way you solve any weak acid problem.

We will need to find the K_a of ammonium ion by looking at the K_b of its conjugate base ... ammonia.

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

Since $K_a \times K_b = 1.0 \times 10^{-14}$ for conjugate pairs,

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

Species	[Initial]	Δ	[Equilibrium]
NH_3	0	$+x$	x
H_3O^+	0	$+x$	x
NH_4^+	0.100	$-x$	$0.100 - x$

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

$$\begin{array}{l} \downarrow x \ll 0.100 \\ \text{so } 0.100 - x \approx 0.100 \end{array}$$

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

$$x = 7.45 \times 10^{-6}$$

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

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

Compare:

pH = 1.00 for 0.100 M strong acid

pH = 2.17 for 0.100 M nitrous 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:

Na^+ : Not a B-L acid (no H^+ to donate). Not likely to be a B-L base (H^+ acceptor) either due to its positive charge.

$\text{C}_2\text{H}_3\text{O}_2^-$: Has hydrogens, so could conceivably be a B-L acid. It's probably a proton acceptor, though, due to the negative charge.



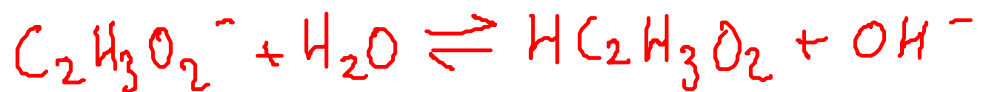
ACETIC ACID ... a well-known WEAK ACID. It's stable in water, so we expect that acetate ion should function as a BASE.

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

K_b for acetate ion isn't listed in our chart, but we can find K_a for acetic acid (its conjugate) on page A-13

$$K_{a, \text{HC}_2\text{H}_3\text{O}_2} = 1.7 \times 10^{-5}; \text{ So } K_{b, \text{C}_2\text{H}_3\text{O}_2^-} = \frac{1.0 \times 10^{-14}}{1.7 \times 10^{-5}}$$

$$K_{b, \text{C}_2\text{H}_3\text{O}_2^-} = 5.88 \times 10^{-10}$$



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

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

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

$x \ll 0.100$

So $0.100-x = 0.100$

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

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

We need pH, but we've calculated HYDROXIDE concentration. Remember to convert it at the end!

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

$$\text{pOH} = 5.12$$

Convert to pH

$$pOH = 5.12$$

Since $pH + pOH = 14.00$

$$pH = 8.88$$

Compare:

pH = 7.00 for pure distilled water

pH = 11.13 for 0.100 M ammonia

pH = 13.00 for 0.100 M NaOH (strong base)

0.100 M NaCl, Find pH



Check the ions formed by the salt to see if they're acidic or basic...

Na^+ : Not a B-L acid since it has no protons (H^+) to donate. Not likely to be B-L base either - due to its positive charge.

Cl^- : Not a B-L acid (no H^+), but it MIGHT be able to accept protons.

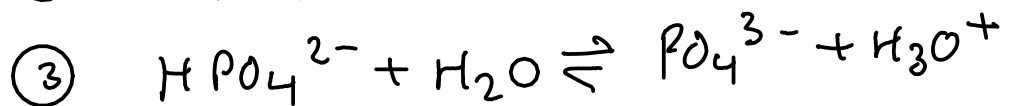
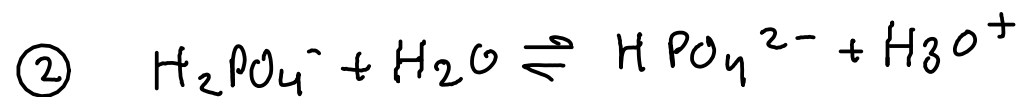
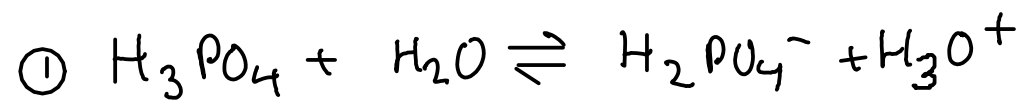


This is hydrochloric acid ... a well-known STRONG ACID. It completely ionizes in water, which means that the chloride ion is not able to hang on to an accepted proton very well. In other words, chloride ion doesn't function as a base ... and should be neutral.

Since neither ion affects pH, the pH will be set by the water equilibrium alone, and this solution will have a pH of 7.00 - same as the pH of distilled water.

Find pH of 0.10 M H_3PO_4

... what's special about phosphoric acid?



Phosphoric acid has THREE acidic protons!

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

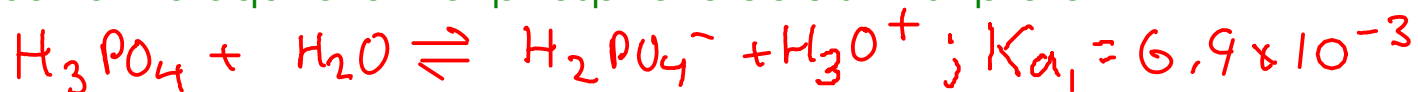
$$K_{a2} = 6.2 \times 10^{-8}$$

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

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]	Δ	[Equilibrium]
H_3PO_4	0.10	-x	0.10 - x
H_2PO_4^-	0	+x	x
H_3O^+	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!)

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

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

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

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

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

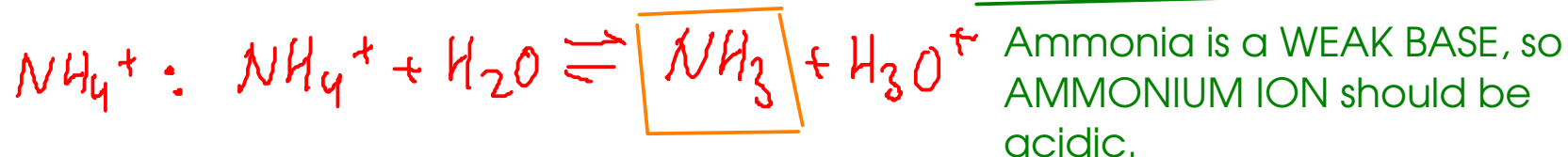
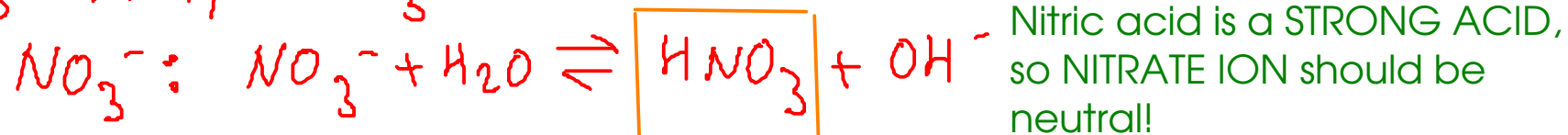
Discard the negative root. 'x' can't be less than zero (it's equal to two of the concentrations!)

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

$$\text{pH} = 1.64$$

171 Find the pH of a solution prepared by dissolving 3.00 g of ammonium nitrate solid into enough water to make 250. mL of solution.

Find out the nature of the salt: Acidic? Basic? Neutral?



$$K_{a, \text{NH}_4^+} = \frac{[\text{NH}_3][\text{H}_2\text{O}]}{[\text{NH}_4^+]}$$

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

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

$$\text{So } K_{a, \text{NH}_4^+} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10}$$

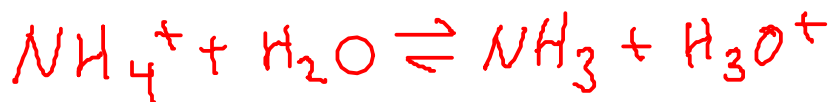
To set this problem up, we'll need to calculate the INITIAL concentrations of each species - then we can make our usual equilibrium chart...

3.00 g NH_4NO_3 in 0.250 L solution

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

$$\begin{aligned} \text{NH}_4\text{NO}_3 : & \text{N} : 2 \times 14.01 \\ & \text{H} : 4 \times 1.008 \\ & \text{O} : 3 \times 16.00 \\ & \hline & 80.052 \text{ g/mol} \end{aligned}$$

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



$$K_{a1, \text{NH}_4^+} = \frac{[\text{NH}_3][\text{H}_3\text{O}^+]}{[\text{NH}_4^+]}$$

$$[\text{NH}_4\text{NO}_3]_{\text{nominal}} = 0.1499025633 \text{ M}$$

Species	[Initial]	Δ	[Equilibrium]
NH_4^+	0.14990	$-x$	$0.14990 - x$
NH_3	0	$+x$	x
H_3O^+	0	$+x$	x

Solve:

$$\frac{x^2}{0.14990 - x} = 5.56 \times 10^{-10}$$

$$\downarrow x \ll 0.14990$$

$$\frac{x^2}{0.14990} = 5.56 \times 10^{-10}$$

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

$$\text{pH} = 5.04$$

This pH seems reasonable for an acidic salt of this concentration.

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 .

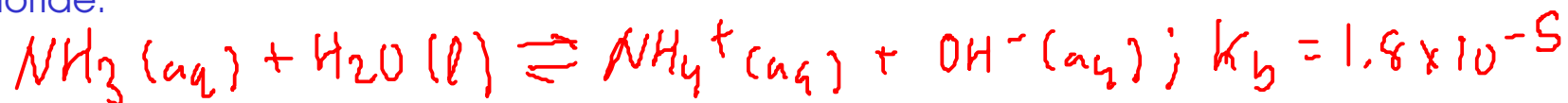
What would happen to the pH if we dissolved ammonium chloride into the solution?



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}	Δ	{Equilibrium}
NH_3	0.10	-x	0.10 - x
NH_4^+	0.10	+x	0.10 + x
OH^-	0	+x	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 $x \ll 0.10$

$$0.10 - x \approx 0.10$$

$$0.10 + x \approx 0.10$$

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

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

$$\text{pOH} = -\log_{10}(1.8 \times 10^{-5}) = 4.74$$

$$\text{pH} = 9.26$$

The common-ion effect suppresses the ionization of the ammonia to an extent, lowering the pH relative to the original ammonia solution.

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.