Chapter 12

Determine the pH of a 0.20M NH₃ solution. Then determine the pH of a solution that is 0.20M NH₃ and also 0.30M NH₄Cl. What do you notice?

A) \[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

\[
\begin{array}{c}
\text{ICE} \\
0.20 - x \\
0 + x \\
0 + x \\
\end{array}
\]

\[
E \ 0.20 - x \\
\ \\
x \\
\ \\
\ \\
\]

\[
K_b = 1.8 \times 10^{-5} \approx \frac{x^2}{0.20} \Rightarrow x = 1.897 \times 10^{-3} M
\]

\[
14 - (-\log x) = 11.3
\]

B) What do you think will happen?

\[
\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-
\]

\[
\begin{array}{c}
\text{ICE} \\
0.20 - x \\
0.30 + x \\
0 + x \\
\end{array}
\]

\[
E \ 0.20 - x \\
\ \\
0.30 + x \\
\x \\
\ \\
\]

\[
K_b = 1.8 \times 10^{-5} = \frac{(0.30+x) \times 0.30x}{(0.20-x)} \approx \frac{0.30x}{0.20}
\]

\[
x = 1.2 \times 10^{-5}
\]

\[
14 - (-\log x) = 9.1
\]

Lower pH = less effect from base
Chapter 12

Determine the pH of a 0.20M NH₃ solution. Then determine the pH of a solution that is 0.20M NH₃ and also 0.30M NH₄Cl. What do you notice? Skip showing assumption check.
Henderson–Hasselbach Derivation

Notice a pattern? Let's do this generally

\[ HA \Rightarrow H^+ + A^- \]

\[ I [HA]_o \quad 0 [A^-]_o \]
\[ C -x \quad +x \quad +x \]
\[ E [HA]_e -x \quad x [A^-]_e +x \]

What does \( x \) actually equal?

\[ \frac{[H^+]}{[HA]_e} \]

So \(-\log x = pH\) lets solve for this

get \( x \) alone & take \(-\log\) of both sides

\[ MUA \quad Ka = \frac{x[A^-]_o}{[HA]_o} \rightarrow x = \frac{Ka[A^-]_o}{[HA]_o} \]

take \(-\log\) both sides

\[-\log x = -\log \left( \frac{Ka [A^-]_o}{[HA]_o} \right) \]

\[ pH = -\log Ka - \log \left( \frac{[A^-]_o}{[HA]_o} \right) \]

\[ pH = pKa + \log \left( \frac{[A^-]_o}{[HA]_o} \right) \]

H H equation
Henderson Hasselbalch Derivation:

Notice a pattern? Let's do this generally for an acid.

\[ HA \rightleftharpoons H^+ + A^- \]
Calculate the pH of the solution that results from mixing 0.200L of 0.050M \((CH_3)_2NH\) with 0.320L of 0.040M \((CH_3)_2NH_2Cl\)

\[ K_b = 5.88 \times 10^{-4} \Rightarrow pK_b = 3.23 \Rightarrow pK_a = 10.77 \]

\[(CH_3)_2NH + H_2O \leftrightarrow (CH_3)_2NH_2^+ + OH^- \]

\[(CH_3)_2NH \Rightarrow 0.200L \times \left(\frac{0.050 \text{ mol}}{L}\right) = 0.010 \text{ mol} \]

\[(CH_3)_2NH_2^+ \Rightarrow 0.320L \times \left(\frac{0.040 \text{ mol}}{L}\right) = 0.0128 \text{ mol} \]

\[ pH = pK_a + \log \left(\frac{[H_3O^+]}{[CH_3_2NH_2^+]}\right) = 10.77 + \log \left(\frac{0.010}{0.0128}\right) = 10.7 \]

**Be Careful**

\[ \text{Use } pK_a \]

You try: Calculate the pH of the solution that results from mixing 72.0mL of 0.015M \((CH_3)_2NH\) with 20mL of 0.200M \((CH_3)_2NH_2Cl\)

\[ 0.072L \times \left(\frac{0.015 \text{ mol}}{L}\right) = 0.00108 \text{ mol} \]

\[ 0.020L \times \left(\frac{0.200 \text{ mol}}{L}\right) = 0.004 \text{ mol} \]

\[ pH = 10.77 + \log \left(\frac{0.00108}{0.004}\right) = 10.2 \]
Calculate the pH of the solution that results from mixing 0.200L of 0.050M $(\text{CH}_3)_2\text{NH}$ with 0.320L of 0.040M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$

$K_b = 5.88 \times 10^{-4}$

You try: Calculate the pH of the solution that results from mixing 72.0mL of 0.015M $(\text{CH}_3)_2\text{NH}$ with 20mL of 0.200M $(\text{CH}_3)_2\text{NH}_2\text{Cl}$

$K_b = 5.88 \times 10^{-4}$
The pH of blood plasma is 7.40, assuming the principal buffer system is HCO₃⁻ and H₂CO₃ find the ratio of HCO₃⁻ and H₂CO₃.

\[
\text{pH} = pK_a + \log \frac{[\text{H}^+]}{[\text{H}_2\text{CO}_3]}
\]

\[
\text{pH} = -\log (4.2 \times 10^{-7}) + \log \frac{\text{HCO}_3^-}{\text{H}_2\text{CO}_3}
\]

\[
\text{pH} = \log (7.4/6.38) = 10^{1.02} = 10.5
\]

\[
10.5 \times \text{more base} = \text{better at buffering}
\]
The pH of blood plasma is 7.40. Assuming the principal buffer system is $\text{HCO}_3^-$ and $\text{H}_2\text{CO}_3$ find the ratio of $\text{HCO}_3^-$ and $\text{H}_2\text{CO}_3$. Is it better at buffering acid or base?
Calculate the pH of 1.00L of the buffer 1.00M CH₃COONa and 1.00M CH₃COOH

A) before and after the addition of B) 0.080 mol NaOH or C) 0.120 mol HCl

A) \[ pH = pK_a + \log \frac{[A^-]}{[HA]} \]

\[ pH = pK_a + \log \frac{0}{0} \]

\[ pH = pK_a = -\log 1.8 \times 10^{-5} = 4.74 \]

B) \[ CH_3COOH + OH^- \rightarrow CH_3COO^- \]

\[
\begin{array}{c|c|c|c}
| & 1 \text{ mol} & 0.080 \text{ mol} & 1 \text{ mol} \\
-0.080 \text{ mol} & 0.080 \text{ mol} & +0.030 \text{ mol} \\
0.92 & 0 & 1.08 \\
\end{array}
\]

\[ pH = pK_a + \log \frac{[A^-]}{[HA]} = 4.74 + \log \frac{0.92}{0.88} = 4.81 \]

C) \[ CH_3COO^- + H^+ \rightarrow CH_3COOH \]

\[
\begin{array}{c|c|c|c}
| & 1 \text{ mol} & 0.12 \text{ mol} & 1 \text{ mol} \\
-0.12 & -0.12 & +0.12 \\
0.88 \text{ mol} & 0 & 1.12 \text{ mol} \\
\end{array}
\]

\[ pH = 4.74 + \log \frac{0.88}{1.12} = 4.64 \]
Calculate the pH of 1.00L of the buffer 1.00M CH₃COONa and 1.00M CH₃COOH

A) 

before and after the addition of B) 0.080 mol NaOH or

C) 0.120 mol HCl
A 10.0 mL solution of 0.300M NH₃ is titrated with a 0.200M HCl solution. Calculate the pH after the following additions of the HCl solution. We will solve this problem using approach 1:

\[
0.00 \text{ mL, } 10.0 \text{ mL, } 15.0 \text{ mL, } 30.0 \text{ mL}
\]

Find eq. \( m_1 v_1 = m_2 v_a \)

\[
0.300 \times 10.0 \text{ mL} = 0.200 \times v_a
\]

\[
v_a = 15 \text{ mL}
\]

\[0.0 \text{ mL} - \text{ this is just a weak base problem using normal methods. I'll leave this to old solutions posted online.}\]

\[\begin{align*}
&\text{A} \quad \text{NH}_3 + \text{H}_2\text{O} \rightarrow \text{NH}_4^+ + \text{OH}^- \\
&\text{I} \quad 0.300 \\
&\text{C} \quad x \\
&\text{E} \quad 0.300 - x
\end{align*}\]

\[
K_b = 1.8 \times 10^{-5} = \frac{x^2}{0.300 - x} \times \frac{x^2}{0.300}
\]

\[
x = 2.32 \times 10^{-3} \text{ M}
\]

\[
\text{pH} = 14 + \log \frac{x}{\text{Moles}} = 11.4
\]

\[
\text{Method 1 - Know you are before equivalence + use HH}
\]

\[
\text{pH} = pK_a + \log \left( \frac{0.003 - 0.002}{0 + 0.002} \right)
\]

\[
pK_a = 9.26 - (\log 1.8 \times 10^{-5}) = 9.26 + \log \left( \frac{0.001}{0.002} \right)
\]

\[
\text{pH} = 9.26 + \log \left( \frac{0.001}{0.002} \right) = 8.95
\]

\[
\text{Method 2 - Know that HCl will react with base read it then see where you have}
\]

\[
\text{NH}_3 + \text{HCl} \rightarrow \text{NH}_4^+ + \text{Cl}^-
\]

\[
0.003 \quad 0.002 \quad \text{OH}
\]

\[
0.002 \quad 0 \quad 0.002 \quad \text{It's a buffer use HH}
\]

\[
\text{pH} = 9.26 + \log \left( \frac{0.001}{0.002} \right) = 8.95
\]
A 10.0 mL solution of 0.300M NH₃ is titrated with a 0.200M HCl solution. Calculate the pH after the following additions of the HCl solution. We will solve this problem using approach 1:

0.0 mL, 10.0 mL, 15.0 mL, 30.0 mL
Method 1
@ equivalence so all base is converted to an acid:

\[ \text{Dilution calculation} \]

\[ 10.0 \times 0.30 = 15.0 \text{mL} \]

\[ M = \frac{0.12}{0.12} \text{M} \]

\[ H^+ + A^- \]

\[ 0.12 \times 0 \times 0 \text{ molality} \]

\[ 0.12 - x \times x \]

\[ K_a = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.12} \Rightarrow x = 8.17 \times 10^{-6} \]

\[ \text{pH} = -\log x = 5.09 \]

Method 2 - react acid & base

\[ NH_3 + H^+ \rightarrow NH_4^+ \]

\[ 0.003 \quad 0.003 \quad 0 \]

\[ -0.003 \quad -0.003 \quad +0.003 \quad \text{reactions} \]

\[ 0 \quad 0 \quad 0.003 \]

\[ \text{it's a weak acid - make an ice chart & fill into Ka} \]

\[ NH_4^+ + H_2O \rightarrow H_3O^+ + NH_3 \]

\[ 0.12M \times 0 \times 0 \]

\[ 0.12M - x \times x \]

\[ K_a = \frac{10^{-14}}{1.8 \times 10^{-5}} = \frac{x^2}{0.12} \Rightarrow x = 8.17 \times 10^{-6} \]

\[ \text{pH} = -\log x = 5.09 \]

Method 1 - Know you are past equivalence + only excess Strong Acid

\[ 30.0 - 15.0 = 15.0 \text{mL} \]

\[ \text{Postequivalence} \]

\[ m_1 \times V_1 = m_2 \times V_2 \]

\[ 30 + 10 \]

\[ (0.200)(15) = m_2(40) \]

\[ m_2 = 0.075 \]

\[ \text{pH} = -\log [H^+] \]

\[ = 1.12 \]

Method 2 - react then see what you have

\[ NH_3 + H^+ \rightarrow NH_4^+ \]

\[ 0.003 \quad 0.004 \quad 0 \]

\[ -0.003 \quad -0.003 \quad +0.003 \quad \text{only strong matter} \]

\[ \log \left( \frac{0.003}{0.04} \right) = 1.12 \]

\[ \frac{(30.0 \pm 10.0 \pm mL)}{1000 \text{mM}} \]
The molar solubility of MnCO₃ is 4.2x10⁻⁶M. What is the Kₚₚ?

\[ \text{MnCO₃} \rightleftharpoons \text{Mn}^{2+} + \text{CO}_3^{2-} \]

\[ K_\text{sp} = [\text{Mn}^{2+}] [\text{CO}_3^{2-}] = 8 \times 10^{-6} \]

\[ x = 4.2 \times 10^{-6} \]

\[ K_\text{sp} = (4.2 \times 10^{-6})^2 = 1.8 \times 10^{-11} \]

If Aluminum Sulfate Ksp is 9.83x10⁻¹⁰, what is the molar solubility?

\[ \text{Al}_2(\text{SO}_4)_3 \rightleftharpoons 2\text{Al}^{3+} + 3\text{SO}_4^{2-} \]

\[ K_\text{sp} = [\text{Al}^{3+}]^2 [\text{SO}_4^{2-}] \]

\[ 9.83 \times 10^{-10} = (2s)^2 (3s)^3 \]

\[ 9.83 \times 10^{-10} = 4(s^2)(2)(3s^3) \]

\[ 9.83 \times 10^{-10} = 10.8s^5 \]

\[ s = 6.19 \times 10^{-3} \text{M} \]

Watch your coefficients. Especially if you are skipping the ice chart!

Remember the coefficients get the exponents too.

Use X or S, I like X better because S and 5 look similar if you (or I) get sloppy with handwriting.
The molar solubility of MnCO₃ is $4.2 \times 10^{-6}$ M. What is the $K_{sp}$?

If Aluminum Sulfate $K_{sp}$ is $9.83 \times 10^{-10}$, what is the molar solubility?
How many grams of CaCO₃ will dissolve in 3.0x10⁻³ mL of 0.050 M Ca(NO₃)₂. The K_sp is 8.7x10⁻⁹.

\[ \text{CaCO}_3 \rightleftharpoons \text{Ca}^{2+} + \text{CO}_3^{2-} \]

<table>
<thead>
<tr>
<th>I</th>
<th>0.050</th>
<th>0</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>+x</td>
<td>+y</td>
</tr>
<tr>
<td>E</td>
<td>0.050x</td>
<td>x</td>
</tr>
</tbody>
</table>

\[ K_{sp} = 8.7 \times 10^{-9} = (x)(0.050+x) \]

\[ x(0.050) \]

\[ x = 1.74 \times 10^{-7} \text{mol/L} \rightarrow \text{convert to grams} \]

\[ 1.74 \times 10^{-7} \text{mol/L} \times 3 \times 10^{-6} \text{L} \times 100.089 \text{g/mol} \]

\[ = 5.2 \times 10^{-11} \text{g} \]

Calculate the molar solubility of AgCl in a 1.00L solution containing 10.0g of dissolved CaCl₂. \( K_{sp} = 1.6 \times 10^{-10} \)

\[ K_{sp} = [\text{Ag}^+] [\text{Cl}^-] = 1.8 \times 10^{-10} \]

\[ 10.0 \text{ g} \left( \frac{1 \text{ mol}}{110.98 \text{ g}} \right) = 0.090 \text{ mol CaCl}_2 = 0.1802 \text{ M Cl}^- \]

\[ K_{sp} = [\text{Ag}^+] [0.1802 + \text{Cl}^-] = x(0.1802 + x) \approx 0.1802x \]

\[ 1.8 \times 10^{-10} = 0.1802x \]

\[ x = \text{molar solubility} = 9.99 \times 10^{-10} \text{ M} \]
How many grams of CaCO₃ will dissolve in 3.0x10⁻³ mL of 0.050 M Ca(NO₃)₂? The Kₛₚ is 8.7x10⁻⁹.

Calculate the molar solubility of AgCl in a 1.00L solution containing 10.0g of dissolved CaCl₂. Kₛₚ = 1.6x10⁻¹⁰
If 20.0 mL of 0.10 M Ba(NO₃)₂ are added to 50.0 mL of 0.10 M Na₂CO₃ will BaCO₃ precipitate?

\[ \text{BaCO}_3 \rightarrow \text{find } [\text{Ba}^{2+}] \text{ and } [\text{CO}_3^{2-}] \]

\[ \text{Ba}^{2+} \rightarrow \text{finding}[\text{Ba}^{2+}] \]

\[ 20.0\text{mL} \times 0.10\text{M} = m_2 \times 0.700\text{mL} \]
\[ m_2 = 0.029 \]

\[ 50.0\text{mL} \times 0.10\text{M} = m_2 \times 0.700\text{mL} \]
\[ m_2 = 0.070 \text{M} \]

Check to see if \( Q > K \) yes if \( Q < K \) no

\[ Q = (0.029)(0.070) = 2.03 \times 10^{-3} \]

\[ K = 8.1 \times 10^{-9} \]

\[ Q > K \]

yes a precipitate will form

You try (with lots of help from me 😊): A volume of 75 mL of 0.060 M NaF is mixed with 25 mL of 0.15M Sr(NO₃)₂. Calculate the concentrations in the final solution of NO₃⁻, Na⁺, and Sr²⁺. F: \( K_f \text{ for } \text{SrF}_2 = 2.0 \times 10^{-10} \)
If 20.0 mL of 0.10 M Ba(NO\textsubscript{3})\textsubscript{2} are added to 50.0 mL of 0.10M Na\textsubscript{2}CO\textsubscript{3} will BaCO\textsubscript{3} precipitate?

\( K_{sp} = 8.1 \times 10^{-9} \)
A volume of 75 mL of 0.060 M NaF is mixed with 25 mL of 0.15M Sr(NO₃)₂. Calculate the concentrations in the final solution of NO₃⁻, Na⁺, and Sr²⁺.

\( \text{K}_\text{sp} \text{ for SrF}_2 = 2.0 \times 10^{-10} \)

**Tells us that SrF₂ isn't very soluble**

All other combinations are

**Do dilution calculations** - \( M_1 \cdot V_1 = M_2 \cdot V_2 \) for each -

\[
\text{NaF} = \frac{75 \text{mL}(0.060 \text{M})}{100 \text{mL}} = 0.045 \text{M NaF} \\
\text{Sr(NO₃)₂} = \frac{25 \text{mL}(0.15 \text{M})}{100 \text{mL}} = 0.0375 \text{M Sr(NO₃)₂} \\
\]

\( \text{NO}_3^- \) and \( \text{Na}^+ \) are spectator ions - they won't react so we can figure those out:

\[
\text{NaF} \rightarrow 1 \text{Na}^+ \text{ per molecule so } 0.045 \text{ M NaF} = 0.045 \text{ M Na}^+ \\
\text{Sr(NO₃)₂} \rightarrow 2 \text{ NO}_3^- \text{ per molecule so } 0.0375 \text{ M Sr(NO₃)₂} = 0.075 \text{ M NO}_3^- \\
\]

**Find Q for SrF₂ to see if precipitates**

\[
Q = (0.045)(0.0375) = 1.6875 \times 10^{-3} > \text{K} \\
F \quad \text{Sr}^{2+} \quad \text{by a lot} \\
\]

Two ions in excess not just 1. How can we do this?
- React till one goes to zero (like a limiting reagent)
- Then treat as common ion effect

**Solvability**

\[
\text{Sr}^{2+} + 2F^- \rightarrow \text{SrF}_2 \\
0.0375 \quad 0.045 \\
-0.045/2 \quad -0.045 \\
0.015 \quad 0 \\
\]

- \( 0.045 \text{ mol L}^-1 \text{ F}_2 \) \( \Rightarrow \) \( 0.045 \text{ mol L}^-1 \text{ SrF}_2 \)

\[
\text{SrF}_2 \Rightarrow \text{Sr}^{2+} + 2F^- \\
0.015 \quad 0 \quad + x \quad 2x \\
0.015 + x \quad 2x \\
\]

\[
\text{K}_\text{sp} = 2.0 \times 10^{-10} = (0.015 + x)(2x)^2 \\
2 \times 0.015(4)(x^2) \\
\]

\[
x \approx 5.77 \times 10^{-5} \\
\text{Sr}^{2+} = 0.015 + x = 0.015M \\
F = 2x = 1.155 \times 10^{-4} = 1.2 \times 10^{-4} \text{ M} \\
\]
A volume of 75 mL of 0.060 M NaF is mixed with 25 mL of 0.15M Sr(NO₃)₂. Calculate the concentrations in the final solution of NO₃⁻, Na⁺, and Sr²⁺, F⁻. (Kₛₚ for SrF₂ = 2.0x10⁻¹⁴). And how many moles of SrF₂ is formed?