Polyprotic Neutralization Reactions: *Not* 1:1 Stoich (yay?)

Both methods of solving (stoichiometry AND the shortcut) still work! There's just a slight twist. ☺

{in mL}

Example: What volume of 4.65 M $Ba(OH)_2$ is needed to neutralize 91 mL of 1.80 M HBr?

1. **Stoichiometry**: $\underline{1}\ Ba(OH)_{2\,(aq)} + \underline{2}\ HBr_{(aq)} \rightarrow \underline{2}\ H_2O_{(l)} + \underline{1}\ BaBr_{2\,(aq)}$

$$1.80\,M \times 0.091\,L = 0.1638\text{ mol HBr} \times \frac{1\text{ mol }Ba(OH)_2}{2\text{ mol HBr}} = 0.0819\text{ mol }Ba(OH)_2$$

$$V_b = \frac{mol}{M} = \frac{0.0819\text{ mol}}{4.65\,M} = 0.01761\,L \Rightarrow \boxed{18\text{ mL}}$$

2. **Shortcut**: Now your equation looks like

$$M_{H^+}V_a = M_{OH^-}V_b$$

Why the change? If an acid and/or base are polyprotic,

$$\text{moles(acid)} \neq \text{moles}(H^+) = \text{moles}(OH^-) \neq \text{moles(base)}$$

Note: If either the base or acid is monoprotic, you can keep that calculation the same as the original shortcut.

monoprotic acid

$$M_a V_a = M_{OH^-} V_b$$

$$(1.80\,M)(91\,mL) = (2 \times 4.65\,M)V_b$$

b/c $Ba(OH)_{\underline{\underline{2}}}$

$$V_b = \frac{1.80 \times 91}{2 \times 4.65} = \boxed{18\text{ mL}}$$

Not a valid FR answer!
On FR, stoich required if not 1:1

Now you try! Choose your favorite method. ☺

1. Calculate the molarity of an $Al(OH)_3$ solution if 32.5 mL of it is needed to neutralize 21 mL of 3.5 M $HClO_4$.

$$M_a V_a = M_{OH^-} V_b$$

$$(3.5\ M)(21\ mL) = M_{OH^-}(32.5\ mL)$$

$$M_{OH^-} = \frac{3.5 \times 21}{32.5} = 2.26\ M\ OH^- \times \frac{1\ Al(OH)_3}{3\ OH^-} = \boxed{0.75\ M\ Al(OH)_3}$$

2. Calculate the volume (in mL) of 1.20 M H_3PO_4 solution needed to neutralize 250 mL of 0.75 M $Ca(OH)_2$.

$$M_{H^+} V_a = M_{OH^-} V_b$$

$$(3 \times 1.20\ M) V_a = (2 \times 0.75\ M)(250\ mL)$$

$$V_a = \frac{2 \times 0.75 \times 250}{3 \times 1.20} = 104\ mL = \boxed{1.0 \times 10^2\ mL}$$

Multiple Choice Practice

1. 0.60 M HNO_3 was used to neutralize 15 mL of 0.30 M $Sr(OH)_2$. What volume of HNO_3 was needed?

   a. 7.5 mL   (b.) 15.0 mL   c. 22.5 mL   d. 30.0 mL

$$M_a V_a = M_{OH^-} V_b$$

$$(0.60\ M) V_a = (2 \times 0.30\ M)(15\ mL) \quad \Big\} \quad V_a = \frac{(2 \times 0.3)(15)}{(0.6)} = 15$$

2. The complete neutralization of 15.0 mL of KOH requires 0.025 mol H_2SO_4. The [KOH] was:

   a. 1.50 M   b. 1.67 M   (c.) 3.33 M   d. 6.67 M

$$mol_{H^+} = M_b V_b$$

$$2 \times 0.025\ mol = M_b(0.015\ L) \Rightarrow M_b = \frac{0.050\ mol}{0.015\ L} = \frac{50}{15} = \frac{10}{3} = 3.33$$

3. During a titration, what volume of 0.500 M KOH is necessary to completely neutralize 10.0 mL of 2.00 M $HC_2H_3O_2$?

   a. 10.0 mL   b. 20.0 mL   c. 25.0 mL   (d.) 40.0 mL

$$M_a V_a = M_b V_b$$

$$(2.00\ M)(10.0\ mL) = (0.500\ M) V_b \Rightarrow V_b = \frac{2 \times 10.0}{0.500} = \frac{20}{1/2} = 2 \times 20$$

Polyprotic Limiting and Excess Calculations

A fun type of limiting excess problem is determining which conjugate of a polyprotic acid is left over in solution after incomplete neutralization with a base!

If you add strong base in a 1:1 mole ratio with a polyprotic acid, one H^+ will be removed:

10. mL 1.0 M NaOH + 10. mL 1.0 M H_3PO_4 → $H_2PO_4^-$ + H_2O (+ Na^+)

If you add strong base in a 2:1 mole ratio with a polyprotic acid, two H^+'s will be removed:

~~20. mL 1.0 M NaOH + 10. mL 1.0 M H_3PO_4 → HPO_4^- + (x2) H_2O (x2) (+ Na^+)~~

If you add strong base in a 3:1 mole ratio with a polyprotic acid, three H^+'s will be removed:

30. mL 1.0 M NaOH + 10. mL 1.0 M H_3PO_4 → PO_4^{3-} + (x3) H_2O (x3) (+ Na^+)

4. Equal volumes of equimolar NaOH(aq) and H_2CO_3(aq) are mixed. Which of the following best shows the relative concentrations of ions in solution?

   a. $[H_2CO_3] = [HCO_3^-] > [CO_3^{2-}] > [NaOH]$
   b. $[H_2CO_3] > [HCO_3^-] = [CO_3^{2-}] > [NaOH]$
   (c.) $[HCO_3^-] > [CO_3^{2-}] > [H_2CO_3] > [NaOH]$ ← none
   d. $[CO_3^{2-}] > [NaOH] > [H_2CO_3] = [HCO_3^-]$

5. What volume of 0.50 M LiOH would you need to add to 100. mL solution of 1.0 M H_3PO_4 to ensure PO_4^{3-} is the predominant anion in solution?

   a. 150. mL
   b. 300. mL
   (c.) 600. mL
   d. 1000. mL

$$M_{H^+} V_a = M_{OH^-} V_b$$

$$(3.0\,M)(100.\,mL) = (0.50\,M) V_b$$

$$V_b = \frac{3 \times 100}{0.5} = \frac{300}{1/2} = 600$$

Polyprotic Acid Titration

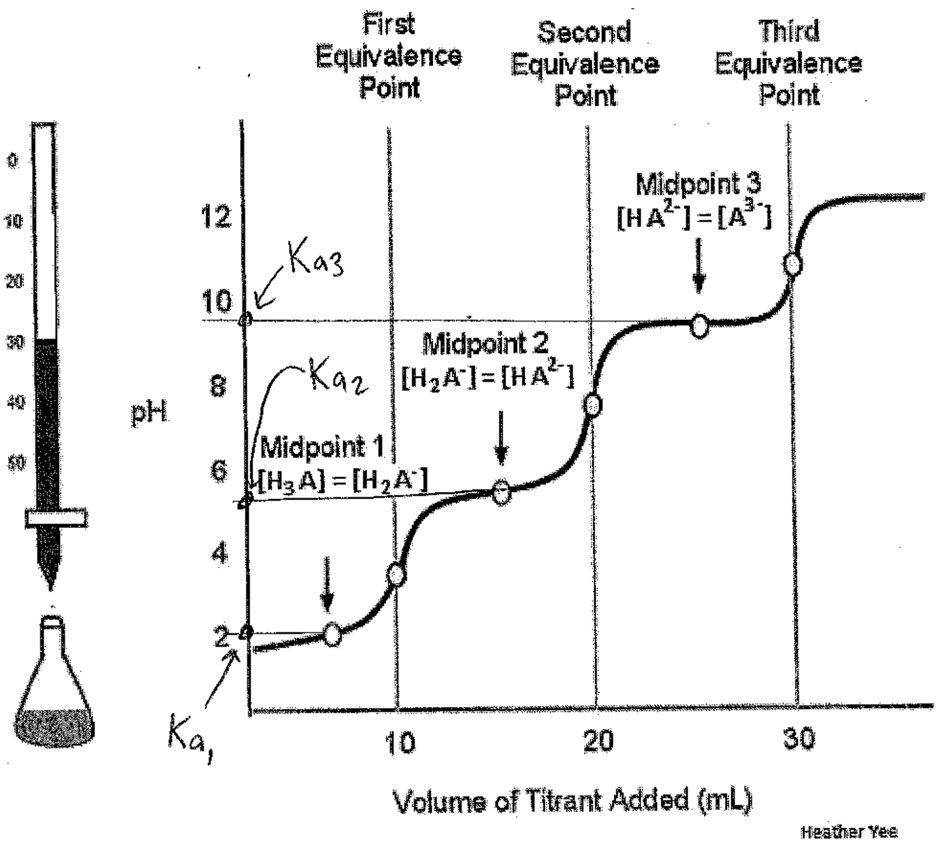
↙ and ½ eq pt if weak!

When titrating a polyprotic acid, each acidic hydrogen will have its own equivalence point!

$H_3A + H_2O \leftrightarrow H_3O^+ + H_2A^-$ $K_{a1} =$ 1×10^{-2}

$H_2A^- + H_2O \leftrightarrow H_3O^+ + HA^{2-}$ $K_{a2} =$ $1 \times 10^{-5.5}$

$HA^{2-} + H_2O \leftrightarrow H_3O^+ + A^{3-}$ $K_{a3} =$ $1 \times 10^{-9.5}$



Note that the volume required to reach the first equivalence point is equal to the volume required to reach the second (and third) equivalence points, because the number of moles of H_3A in the first step determines the number of moles of H_2A^- in the second step, and the number of moles of HA^{2-} in the third step.