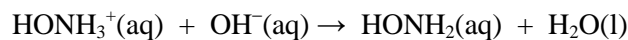
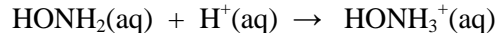
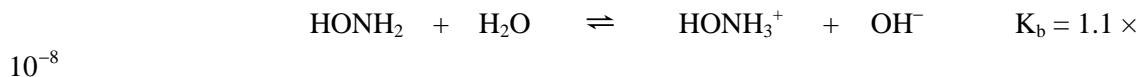


22. Similar to the $\text{HCO}_3^-/\text{CO}_3^{2-}$ buffer discussed in Exercise 21, the $\text{HONH}_3^+/\text{HONH}_2$ buffer absorbs added OH^- and H^+ in the same fashion.



24. a. Weak base problem:

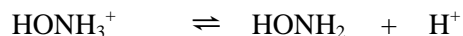


Initial	0.100 M		0	~0
	<i>x</i> mol/L HONH_2 reacts with H_2O to reach equilibrium			
Change	! <i>x</i>	→	+ <i>x</i>	+ <i>x</i>
Equil.	0.100 ! <i>x</i>		<i>x</i>	<i>x</i>

$$K_b = 1.1 \times 10^{-8} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = [\text{OH}^-] = 3.3 \times 10^{-5} \text{ M}; \text{ pOH} = 4.48; \text{ pH} = 9.52 \quad \text{Assumptions good.}$$

- b. Weak acid problem (Cl^- has no acidic/basic properties);



Initial	0.100 M		0	~0
	<i>x</i> mol/L HONH_3^+ dissociates to reach equilibrium			
Change	! <i>x</i>	→	+ <i>x</i>	+ <i>x</i>
Equil.	0.100 ! <i>x</i>		<i>x</i>	<i>x</i>

$$K_a = \frac{K_w}{K_b} = 9.1 \times 10^{-7} = \frac{[\text{HONH}_2][\text{H}^+]}{[\text{HONH}_3^+]} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}$$

$$x = [\text{H}^+] = 3.0 \times 10^{-4} \text{ M}; \text{ pH} = 3.52 \quad \text{Assumptions good.}$$

- c. Pure H_2O , $\text{pH} = 7.00$

- d. Buffer solution where $\text{pK}_a = -\log(9.1 \times 10^{-7}) = 6.04$. Using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = 6.04 + \log \frac{[\text{HONH}_2]}{[\text{HONH}_3^+]} = 6.04 + \log \frac{(0.100)}{(0.100)} = 6.04$$

32. Consider all of the results to Exercises 15.24, 15.28, and 15.30.

Solution	Initial pH	after added acid	after added base
a	9.52	6.64	12.30
b	3.52	1.70	5.44
c	7.00	1.70	12.30
d	6.04	5.86	6.22

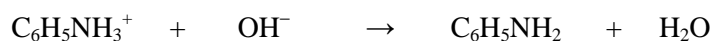
The solution in Exercise 15.24d is a buffer; it shows the greatest resistance to a change in pH when strong acid or base is added. The solution in Exercise 15.24d contains a weak acid (HONH_3^+) and a weak base (HONH_2), which constitutes a buffer solution.

40. a. pK_b for $\text{C}_6\text{H}_5\text{NH}_2 = -\log(3.8 \times 10^{-4}) = 9.42$; pK_a for $\text{C}_6\text{H}_5\text{NH}_3^+ = 14.00 - 9.42 = 4.58$

$$\text{pH} = \text{pK}_a + \frac{[\text{C}_6\text{H}_5\text{NH}_2]}{[\text{C}_6\text{H}_5\text{NH}_3^+]}, \quad 4.20 = 4.58 + \log \frac{0.50 M}{[\text{C}_6\text{H}_5\text{NH}_3^+]}$$

$$-0.38 = \log \frac{0.50 M}{[\text{C}_6\text{H}_5\text{NH}_3^+]}, \quad [\text{C}_6\text{H}_5\text{NH}_3^+] = [\text{C}_6\text{H}_5\text{NH}_3\text{Cl}] = 1.2 M$$

- b. $4.0 \text{ g NaOH} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g}} \times \frac{1 \text{ mol OH}^-}{1 \text{ mol NaOH}} = 0.10 \text{ mol OH}^-$, $[\text{OH}^-] = \frac{0.10 \text{ mol}}{1.0 \text{ L}} = 0.10 M$



Before	1.2 M	0.10 M		0.50 M
Change	-0.10	-0.10	→	+0.10
After	1.1	0		0.60

A buffer solution exists. $\text{pH} = 4.58 + \log \left(\frac{0.60}{1.1} \right) = 4.32$

48. a. No; A solution of a strong acid (HNO_3) and its conjugate base (NO_3^-) is not generally considered a buffer solution.
- b. No; Two acids are present (HNO_3 and HF), so it is not a buffer solution.
- c. H^+ reacts completely with F^- . Since equal volumes are mixed, the initial concentrations in the mixture are 0.10 M HNO_3 and 0.20 M NaF .



Before	0.10 M	0.20 M		0
Change	-0.10	-0.10	→	+0.10

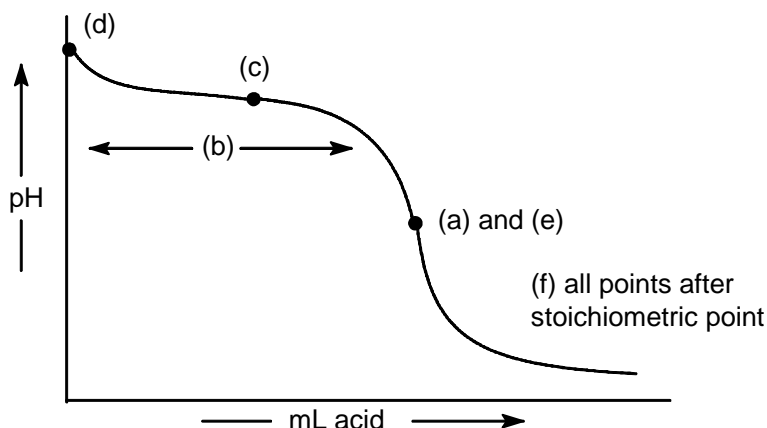
Reacts completely

After 0 0.10 0.10

After H^+ reacts completely, a buffer solution results, i.e., a weak acid (HF) and its conjugate base (F^-) are both present in solution in large quantities.

- d. No; A strong acid (HNO_3) and a strong base (NaOH) do not form buffer solutions. They will neutralize each other to form H_2O .

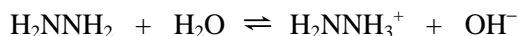
52.



$\text{B} + \text{H}^+ \rightarrow \text{BH}^+$; Added H^+ from the strong acid converts the weak base, B , into its conjugate acid, BH^+ . Initially, before any H^+ is added (point d), B is the dominant species present. After H^+ is added, both B and BH^+ are present and a buffered solution results (region b). At the equivalence point (points a and e), exactly enough H^+ has been added to convert all of the weak base present initially into its conjugate acid, BH^+ . Past the equivalence point (region f), excess H^+ is present. For the answer to b, we included almost the entire buffer region. The maximum buffer region is around the halfway point to equivalence (point c) where $[\text{B}] = [\text{BH}^+]$. Here, $\text{pH} = \text{pK}_a$ which is a characteristic of a best buffer.

56. This is a weak base (H_2NNH_2) titrated by a strong acid (HNO_3). To calculate the pH at the various points, let the strong acid react completely with the weak base present, then see what is in solution.

- a. Only a weak base is present. Solve the weak base equilibrium problem.



Initial	0.100 M	0	~0
Equil.	0.100 - x	x	x

$$K_b = 3.0 \times 10^{-6} = \frac{x^2}{0.100 - x} \approx \frac{x^2}{0.100}, \quad x = [\text{OH}^-] = 5.5 \times 10^{-4} M$$

pOH = 3.26; pH = 10.74; Assumptions good.

b. mmol H_2NNH_2 present = $100.0 \text{ mL} \times \frac{0.100 \text{ mmol } \text{H}_2\text{NNH}_2}{\text{mL}} = 10.0 \text{ mmol } \text{H}_2\text{NNH}_2$

$$\text{mmol } \text{H}^+ \text{ added} = 20.0 \text{ mL} \times \frac{0.200 \text{ mmol } \text{H}^+}{\text{mL}} = 4.00 \text{ mmol } \text{H}^+$$

Let the H^+ from the strong acid react to completion with the best base present (H_2NNH_2).

	H_2NNH_2	+	H^+	\rightarrow	H_2NNH_3^+	
Before	10.0 mmol		4.00 mmol		0	
Change	-4.00 mmol		-4.00 mmol	\rightarrow	+4.00 mmol	Reacts completely
After	6.0 mmol		0		4.00 mmol	

A buffered solution results after the titration reaction. Solving using the Henderson-Hasselbalch equation:

$$\text{pH} = \text{p}K_a + \log \frac{[\text{Base}]}{[\text{Acid}]}, \quad K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-6}} = 3.3 \times 10^{-9}$$

$$\text{pH} = -\log(3.3 \times 10^{-9}) + \log \left(\frac{6.0 \text{ mmol} / V_T}{4.00 \text{ mmol} / V_T} \right) \quad \text{where } V_T = \text{total volume,}$$

which cancels

$$\text{pH} = 8.48 + \log(1.5) = 8.48 + 0.18 = 8.66$$

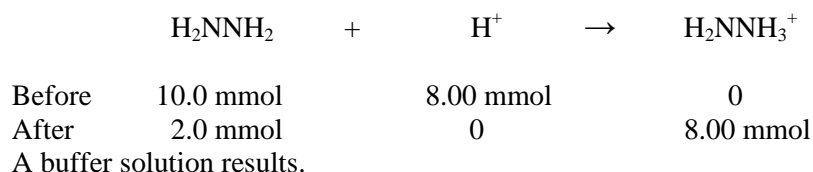
c. mmol H^+ added = $25.0 \text{ mL} \times 0.200 M = 5.00 \text{ mmol } \text{H}^+$

	H_2NNH_2	+	H^+	\rightarrow	H_2NNH_3^+
Before	10.0 mmol		5.00 mmol		0
After	5.0 mmol		0		5.00 mmol

This is the halfway point to equivalence where $[\text{H}_2\text{NNH}_3^+] = [\text{H}_2\text{NNH}_2]$. At this point, $\text{pH} = \text{p}K_a$ (which is characteristic of the halfway point for any weak base/strong acid titration).

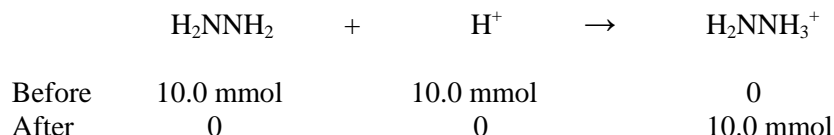
$$\text{pH} = -\log(3.3 \times 10^{-9}) = 8.48$$

d. $\text{mmol H}^+ \text{ added} = 40.0 \text{ mL} \times 0.200 \text{ M} = 8.00 \text{ mmol H}^+$

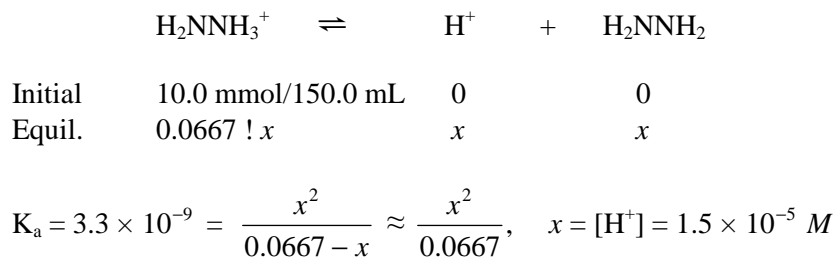


$$\text{pH} = \text{pK}_a + \log \frac{[\text{Base}]}{[\text{Acid}]} = 8.48 + \log \left(\frac{2.0 \text{ mmol} / V_T}{8.00 \text{ mmol} / V_T} \right) = 8.48 + (-0.60) = 7.88$$

e. $\text{mmol H}^+ \text{ added} = 50.0 \text{ mL} \times 0.200 \text{ M} = 10.0 \text{ mmol H}^+$. This is the equivalence point where just enough H^+ has been added to react with all of the weak base present.

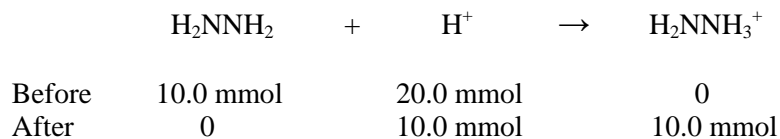


As is always the case in a weak base/strong acid titration, the pH at the equivalence point is acidic because only a weak acid (H_2NNH_3^+) is present (conjugate acids of all weak bases are weak acids themselves). Solving the weak acid equilibrium problem:



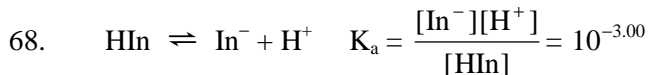
$\text{pH} = 4.82$; Assumptions good.

f. $\text{mmol H}^+ \text{ added} = 100.0 \text{ mL} \times 0.200 \text{ M} = 20.0 \text{ mmol H}^+$



Two acids are present past the equivalence point, but the excess H^+ will determine the pH of the solution since H_2NNH_3^+ is a weak acid. Whenever two acids are present, the stronger acid usually determines the pH.

$$[\text{H}^+]_{\text{excess}} = \frac{10.0 \text{ mmol}}{100.0 \text{ mL} + 100.0 \text{ mL}} = 0.0500 \text{ M}; \quad \text{pH} = 1.301$$



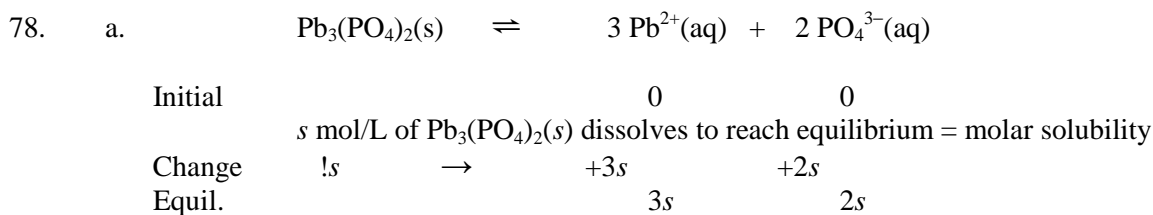
At 7.00% conversion of HIn into In^- , $[\text{In}^-]/[\text{HIn}] = 7.00/93.00$.

$$K_a = 1.0 \times 10^{-3} = \frac{[\text{In}^-]}{[\text{HIn}]} \times [\text{H}^+] = \frac{7.00}{93.00} \times [\text{H}^+], \quad [\text{H}^+] = 1.3 \times 10^{-2} \text{ M}, \quad \text{pH} = 1.89$$

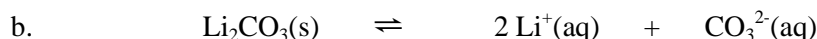
The color of the base form will start to show when the pH is increased to 1.89.

72.	<u>Exercise</u>	<u>pH at eq. pt.</u>	<u>Indicator</u>
	15.58	8.79	phenolphthalein
	15.60	3.27	2,4-dinitrophenol

The titration in 15.60 is not feasible. The pH break at the equivalence point is too small.



$$K_{\text{sp}} = [\text{Pb}^{2+}]^3 [\text{PO}_4^{3-}]^2 = (3s)^3 (2s)^2 = 108 s^5, \quad K_{\text{sp}} = 108(6.2 \times 10^{-12})^5 = 9.9 \times 10^{-55}$$



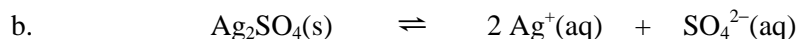
Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		$2s$	s

$$K_{\text{sp}} = [\text{Li}^+]^2 [\text{CO}_3^{2-}] = (2s)^2 (s) = 4s^3, \quad K_{\text{sp}} = 4(7.4 \times 10^{-2})^3 = 1.6 \times 10^{-3}$$



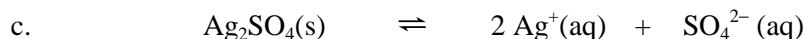
Initial	$s = \text{solubility (mol/L)}$	0	0
Equil.		$2s$	s

$$K_{\text{sp}} = 1.2 \times 10^{-5} = [\text{Ag}^+]^2 [\text{SO}_4^{2-}] = (2s)^2 s = 4s^3, \quad s = 1.4 \times 10^{-2} \text{ mol/L}$$



Initial	$s = \text{solubility (mol/L)}$	0.10 M	0
Equil.		$0.10 + 2s$	s

good. $K_{\text{sp}} = 1.2 \times 10^{-5} = (0.10 + 2s)^2(s) \approx (0.10)^2(s)$, $s = 1.2 \times 10^{-3} \text{ mol/L}$; Assumption



Initial	$s = \text{solubility (mol/L)}$	0	0.20 M
Equil		$2s$	$0.20 + s$

$1.2 \times 10^{-5} = (2s)^2(0.20 + s) \approx 4s^2(0.20)$, $s = 3.9 \times 10^{-3} \text{ mol/L}$; Assumption good.

Note: Comparing the solubilities of parts b and c to that of part a illustrates that the solubility of a salt decreases when a common ion is present.

96. a. AgF b. $\text{Pb}(\text{OH})_2$ c. $\text{Sr}(\text{NO}_2)_2$ d. $\text{Ni}(\text{CN})_2$

All the above salts have anions that are bases. The anions of the other choices are conjugate bases of strong acids. They have no basic properties in water and, therefore, do not have solubilities which depend on pH.

117. $\text{NH}_3 + \text{H}_2\text{O} \rightleftharpoons \text{NH}_4^+ + \text{OH}^-$ $K_b = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$; Taking the \log of the K_b expression:

$$\log K_b = \log [\text{OH}^-] + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}, \quad \log [\text{OH}^-] = \log K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]}$$

$$\text{pOH} = \text{p}K_b + \log \frac{[\text{NH}_4^+]}{[\text{NH}_3]} \quad \text{or} \quad \text{pOH} = \text{p}K_b + \log \frac{[\text{Acid}]}{[\text{Base}]}$$

120. $\text{pH} = \text{p}K_a + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}, \quad 4.00 = \log(1.8 \times 10^{-5}) + \log \frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]}$

$$\frac{[\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} = 0.18; \text{ This is also equal to the mole ratio between } \text{C}_2\text{H}_3\text{O}_2^- \text{ and } \text{HC}_2\text{H}_3\text{O}_2.$$

Let x = volume of 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$ and y = volume of 1.00 M $\text{NaC}_2\text{H}_3\text{O}_2$

$$x + y = 1.00 \text{ L}, \quad x = 1.00 - y$$

$$x (1.0 \text{ mol/L}) = \text{mol HC}_2\text{H}_3\text{O}_2; \quad y (1.00 \text{ mol/L}) = \text{mol NaC}_2\text{H}_3\text{O}_2 = \text{mol C}_2\text{H}_3\text{O}_2^-$$

$$\text{So, } \frac{y}{x} = 0.18 \text{ or } \frac{y}{1.00 - y} = 0.18; \text{ Solving: } y = 0.15 \text{ L so } x = 1.00 - 0.15 = 0.85 \text{ L}$$

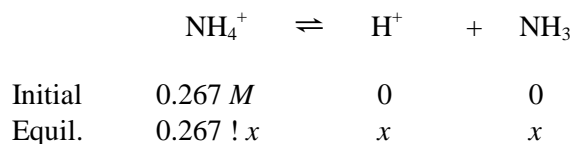
We need 850 mL of 1.00 M $\text{HC}_2\text{H}_3\text{O}_2$ and 150 mL of 1.00 M $\text{NaC}_2\text{H}_3\text{O}_2$ to produce a buffer solution at $\text{pH} = 4.00$.

124. a. Because all acids are the same initial concentration, the pH curve with the highest pH at 0 mL of NaOH added will correspond to the titration of the weakest acid. This is pH curve f.
- b. The pH curve with the lowest pH at 0 mL of NaOH added will correspond to the titration of the strongest acid. This is pH curve a.

The best point to look at to differentiate a strong acid from a weak acid titration (if initial concentrations are not known) is the equivalence point pH. If the $\text{pH} = 7.00$, the acid titrated is a strong acid; if the pH is greater than 7.00, the acid titrated is a weak acid.

- c. For a weak acid-strong base titration, the pH at the halfway point to equivalence is equal to the pK_a value. The pH curve, which represents the titration of an acid with $\text{K}_a = 1.0 \times 10^{-6}$, will have a $\text{pH} = -\log(1 \times 10^{-6}) = 6.0$ at the halfway point. The equivalence point, from the plots, occurs at 50 mL NaOH added, so the halfway point is 25 mL. Plot d has a $\text{pH} \sim 6.0$ at 25 mL of NaOH added, so the acid titrated in this pH curve (plot d) has $\text{K}_a \sim 1 \times 10^{-6}$.
140. $0.400 \text{ mol/L} \times V_{\text{NH}_3} = \text{mol NH}_3 = \text{mol NH}_4^+$ after reaction with HCl at the equiv. point.

$$\text{At the equivalence point: } [\text{NH}_4^+]_0 = \frac{\text{mol NH}_4^+}{\text{total volume}} = \frac{0.400 \times V_{\text{NH}_3}}{1.50 \times V_{\text{NH}_3}} = 0.267 \text{ M}$$



$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10} = \frac{x^2}{0.267 - x} \approx \frac{x^2}{0.267}$$

$$x = [H^+] = 1.2 \times 10^{-5} M; \text{ pH} = 4.92; \text{ Assumption good.}$$