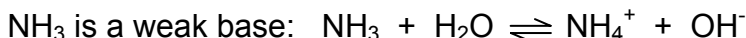


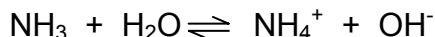
## COMMON ION & BUFFER PROBLEMS KEY

- 1) What is the pH of a solution containing 0.30 M  $\text{NH}_3$  and 0.15 M  $\text{NH}_4\text{NO}_3$ ?

$$K_b \text{ for } \text{NH}_3 = 1.8 \times 10^{-5}$$



$\text{NH}_4\text{NO}_3$  is a salt:  $\text{NH}_4\text{NO}_3 \rightarrow \text{NH}_4^+ + \text{NO}_3^-$ ; thus  $\text{NH}_4^+$  is a "common ion"



	$[\text{NH}_3]$ M	$[\text{H}_2\text{O}]$	$[\text{NH}_4^+]$ M	$[\text{OH}^-]$ M
I	0.30		0.15	0
C	-x		+x	+x
E	0.30 - x		0.15 + x	x

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

Approximation: ignore -x, +x terms:  $1.8 \times 10^{-5} = \frac{(0.15)x}{(0.30)}$

$$x = [\text{OH}^-] = 3.6 \times 10^{-5} \text{ M}$$

$$\text{pOH} = -\log 3.6 \times 10^{-5} = 4.44$$

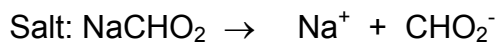
$$\text{pH} = 14 - 4.44 = 9.56$$

$$\text{pH} = 9.56$$

(This problem can also be solved using the  $K_a$  rxn:  $\text{NH}_4^+ \rightleftharpoons \text{NH}_3 + \text{H}^+$ ; if you use this reaction, you must convert  $K_b$  to its corresponding  $K_a$  value.)

- 2) A buffer solution contains 0.20 M  $\text{HCHO}_2$  and 0.30 M  $\text{NaCHO}_2$ . The volume of the solution is 125 mL.  $K_a$  for  $\text{HCHO}_2 = 1.8 \times 10^{-4}$

- a) What is the pH of this buffer solution?



I	0.20	0	0.30
C	-x	+x	+x
E	0.20-x	+x	0.30+x

Approximation: ignore -x, +x terms

$$K_a = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} \Rightarrow 1.8 \times 10^{-4} = \frac{x(0.30)}{(0.20)} \Rightarrow x = [\text{H}^+] = 1.2 \times 10^{-4}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.2 \times 10^{-4} = 3.92$$

$$\text{pH} = 3.92$$

- b) If 50.0 mL of 0.10 M  $\text{NaOH}$  is added to the buffer solution, what is the pH?



$$\text{diluted so recalculate M: } \text{M HCHO}_2 = \frac{(0.20 \text{ M})(125 \text{ ml})}{(175 \text{ ml})} = 0.14 \text{ M}$$

$$\text{M CHO}_2^- = \frac{(0.30 \text{ M})(125 \text{ ml})}{(175 \text{ ml})} = 0.21 \text{ M}; \quad \text{M OH}^- = \frac{(0.10 \text{ M})(50.0 \text{ ml})}{(175 \text{ ml})} = 0.029 \text{ M}$$

neutralization reaction:  $\text{OH}^- + \text{HCHO}_2 \rightarrow \text{CHO}_2^- + \text{H}_2\text{O}$

Initial	0.029	0.14	0.21	
Change	-0.029	-0.029	+0.029	
Final	0	0.11	0.24	

Acid ionization rxn:  $\text{HCHO}_2 \rightleftharpoons \text{H}^+ + \text{CHO}_2^-$

I	0.11	0	0.24
C	-x	+x	+x
E	0.11-x	+x	0.24+x

$$K_a = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} \Rightarrow 1.8 \times 10^{-4} = \frac{x(0.24)}{(0.11)} \Rightarrow x = [\text{H}^+] = 8.25 \times 10^{-5}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 8.25 \times 10^{-5} = 4.08 \quad \text{pH} = 4.08$$

**\*For a buffer solution, pH only rises a little if a small amount of strong base is added.**

c) If 50.0 mL of 0.10 M HCl is added to the buffer solution, what is the pH?

Strong acid:  $\text{HCl} + \text{H}_2\text{O} \rightarrow \text{H}_3\text{O}^+ + \text{Cl}^-$

$$\text{diluted so recalculate M: } M \text{ HCHO}_2 = \frac{(0.20 \text{ M})(125 \text{ ml})}{(175 \text{ ml})} = 0.14 \text{ M}$$

$$M \text{ CHO}_2^- = \frac{(0.30 \text{ M})(125 \text{ ml})}{(175 \text{ ml})} = 0.21 \text{ M}; \quad M \text{ H}^+ = \frac{(0.10 \text{ M})(50.0 \text{ ml})}{(175 \text{ ml})} = 0.029 \text{ M}$$

neutralization reaction:  $\text{H}^+ + \text{CHO}_2^- \rightarrow \text{HCHO}_2$

Initial	0.029	0.21	0.14
Change	-0.029	-0.029	+0.029
Final	0	0.18	0.17

Acid ionization rxn:  $\text{HCHO}_2 \rightleftharpoons \text{H}^+ + \text{CHO}_2^-$

I	0.17	0	0.18
C	-x	+x	+x
E	0.17-x	+x	0.18+x

$$K_a = \frac{[\text{H}^+][\text{CHO}_2^-]}{[\text{HCHO}_2]} \Rightarrow 1.8 \times 10^{-4} = \frac{x(0.18)}{(0.17)} \Rightarrow x = [\text{H}^+] = 1.7 \times 10^{-4}$$

$$\text{pH} = -\log[\text{H}^+] = -\log 1.7 \times 10^{-4} = 3.77 \quad \text{pH} = 3.77$$

**\* For a buffer, pH only drops a little when a small amount of strong acid is added.**

## TITRATION PROBLEMS KEY

1. A 20.00 ml sample of 0.150 M HCl is titrated with 0.200 M NaOH. Calculate the pH of the solution after the following volumes of NaOH have been added: a) 0 mL; b) 10.00 mL; c) 15.0 mL; d) 20.00 mL.

a) 0 ml of NaOH added – only SA is present initially:

For strong acid:  $[H^+] = [HCl] = 0.150 \text{ M HCl}$

$$\text{pH} = -\log[H^+] = -\log(0.150) = \mathbf{0.824}$$

b) 10.00 ml of NaOH

neutralization reaction:  $\text{HCl} + \text{NaOH} \rightarrow \text{NaCl} + \text{H}_2\text{O}$   
SA                      SB

$$\text{moles HCl} = 20.00 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.150 \text{ moles HCl}}{\text{L}} \right) = 3.00 \times 10^{-3} \text{ moles HCl}$$

$$\text{moles NaOH} = 10.00 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.200 \text{ moles NaOH}}{\text{L}} \right) = 2.00 \times 10^{-3} \text{ moles NaOH}$$

After neutralization:

moles excess acid =  $3.00 \times 10^{-3} \text{ moles} - 2.00 \times 10^{-3} \text{ moles} = 1.00 \times 10^{-3} \text{ moles HCl}$

$$\text{M } H^+ = \text{M HCl} = \frac{1.00 \times 10^{-3} \text{ moles}}{0.03000 \text{ L}} = 0.0333 \text{ M}$$

$$\text{pH} = -\log [H^+] = -\log 0.0333 = \mathbf{1.478}$$

c) 15.0 mL of NaOH

From part b, moles HCl =  $3.00 \times 10^{-3} \text{ moles HCl}$

$$\text{moles NaOH} = 15.00 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.200 \text{ moles NaOH}}{\text{L}} \right) = 3.00 \times 10^{-3} \text{ moles NaOH}$$

moles HCl = moles NaOH

at equivalence pt:  $\text{pH} = \mathbf{7.000}$  (for SA/SB titration)

d) 20.00 mL

from part b, moles HCl =  $3.00 \times 10^{-3} \text{ moles HCl}$

$$\text{moles NaOH} = 20.00 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.200 \text{ moles NaOH}}{\text{L}} \right) = 4.00 \times 10^{-3} \text{ moles NaOH}$$

After neutralization:

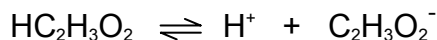
moles excess base =  $4.00 \times 10^{-3} \text{ moles} - 3.00 \times 10^{-3} \text{ moles} = 1.00 \times 10^{-3} \text{ moles NaOH}$

$$\text{M } OH^- = \text{M NaOH} = \frac{1.00 \times 10^{-3} \text{ moles}}{0.040 \text{ L}} = 0.0250 \text{ M } OH^-$$

$$\text{pOH} = -\log 0.0250 = 1.602 \quad \text{pH} = 14 - 1.602 = \mathbf{12.398}$$

2. A 50.0 mL sample of 0.50 M HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> acid is titrated with 0.150 M NaOH. K<sub>a</sub> = 1.8x10<sup>-5</sup> for HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>. Calculate the pH of the solution after the following volumes of NaOH have been added: a) 0 mL; b) 166.7 mL; c) 180.0 mL.

a) 0 ml of base; only a weak acid is initially present so [H<sup>+</sup>] ≠ [HA]



I	0.50	0	0
C	-x	x	x
E	0.50-x	x	x

$$K_a = \frac{[\text{H}^+][\text{C}_2\text{H}_3\text{O}_2^-]}{[\text{HC}_2\text{H}_3\text{O}_2]} \quad 1.8 \times 10^{-5} = \frac{x^2}{0.50}$$

$$[\text{H}^+] = x = \sqrt{0.50(1.8 \times 10^{-5})} = 3.0 \times 10^{-3}$$

$$\text{pH} = -\log 3.0 \times 10^{-3} = \mathbf{2.52}$$

b) 166.7 ml of NaOH are added

from part b, moles HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> = 2.5x10<sup>-2</sup> moles HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

$$\text{moles NaOH} = 166.7 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.150 \text{ moles NaOH}}{\text{L}} \right) = 2.50 \times 10^{-2} \text{ moles NaOH}$$

neutralization: HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> + OH<sup>-</sup> → C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> + H<sub>2</sub>O

I	0.025	0.0250	0	
C	-0.025	-0.025	+0.025	
Final	0	0	0.025	

only acetate remains – a weak base:

$$[\text{C}_2\text{H}_3\text{O}_2^-] = \frac{2.5 \times 10^{-2} \text{ moles}}{0.2167 \text{ L}} = 0.115 \text{ M}$$

base hydrolysis: C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>-</sup> + H<sub>2</sub>O ⇌ HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> + OH<sup>-</sup>

I	0.115		0	0
C	-x		x	x
E	0.115-x		x	x

$$K_b \text{ for } \text{C}_2\text{H}_3\text{O}_2^- = \frac{1 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.6 \times 10^{-10}$$

$$K_b = \frac{[\text{HC}_2\text{H}_3\text{O}_2][\text{OH}^-]}{[\text{C}_2\text{H}_3\text{O}_2^-]} \quad 5.6 \times 10^{-10} = \frac{x^2}{0.115}$$

$$x = [\text{OH}^-] = \sqrt{0.115(5.6 \times 10^{-10})} = 8.0 \times 10^{-6}$$

$$\text{pOH} = -\log 8.0 \times 10^{-6} = 5.10 \quad \text{pH} = 14 - 5.10 = \mathbf{8.90}$$

⇒ At the equivalence point for a WA/SB titration, the pH > 7 due to the OH<sup>-</sup> produced by the conjugate base hydrolysis reaction.

c) 180.0 mL of NaOH are added

from part b, moles HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub> = 2.5x10<sup>-2</sup> moles HC<sub>2</sub>H<sub>3</sub>O<sub>2</sub>

$$\text{moles NaOH} = 180.00 \text{ ml} \left( \frac{1 \text{ L}}{1000 \text{ mL}} \right) \left( \frac{0.150 \text{ moles NaOH}}{\text{L}} \right) = 2.7 \times 10^{-2} \text{ moles NaOH}$$

$$\text{moles excess base} = 2.7 \times 10^{-2} \text{ moles} - 2.5 \times 10^{-2} \text{ moles} = 2.0 \times 10^{-3} \text{ moles NaOH}$$

$$\text{M OH}^- = \text{M NaOH} = \frac{2.0 \times 10^{-3} \text{ moles}}{0.23 \text{ L}} = 8.7 \times 10^{-3} \text{ M OH}^-$$

$$\text{pOH} = -\log 8.7 \times 10^{-3} = 2.06$$

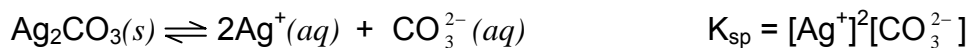
$$\text{pH} = 14 - 2.06 = \mathbf{11.94}$$

\*Excess NaOH remains - this is the primary source of OH<sup>-</sup>. We can neglect the hydrolysis of the conjugate base because this would contribute a relatively small amount of OH<sup>-</sup> compared to the amount that comes directly from the excess NaOH.

## SOLUBILITY PROBLEMS KEY

1. At 25 °C, 0.0349 g of  $\text{Ag}_2\text{CO}_3$  dissolves in 1.0 L of solution. Calculate  $K_{\text{sp}}$  for this salt.

$$\text{solubility} = \frac{0.0349 \text{ g Ag}_2\text{CO}_3}{1.0 \text{ L}} \times \frac{1 \text{ mol Ag}_2\text{CO}_3}{275.8 \text{ g Ag}_2\text{CO}_3} = 1.3 \times 10^{-4} \text{ M Ag}_2\text{CO}_3$$



I		0	0
C		2x	x
E		2x	x

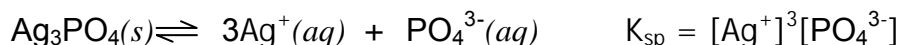
$$x = \text{molar solubility of Ag}_2\text{CO}_3 = 1.3 \times 10^{-4} \text{ M}$$

$$[\text{CO}_3^{2-}] = x = 1.3 \times 10^{-4} \text{ M}$$

$$[\text{Ag}^+] = 2x = 2(1.3 \times 10^{-4} \text{ M}) = 2.6 \times 10^{-4} \text{ M}$$

$$K_{\text{sp}} = [2.6 \times 10^{-4}]^2 [1.3 \times 10^{-4}] = 8.8 \times 10^{-12}$$

2. Silver phosphate,  $\text{Ag}_3\text{PO}_4$ , is an insoluble salt that has a  $K_{\text{sp}} = 1.3 \times 10^{-20}$ .  
a) Calculate the molar solubility of  $\text{Ag}_3\text{PO}_4$  in pure water.



I		0	0
C		3x	x
E		3x	x

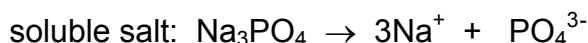
$$K_{\text{sp}} = (3x)^3 x$$

$$1.3 \times 10^{-20} = 27x^4$$

$$x^4 = 4.8 \times 10^{-22}$$

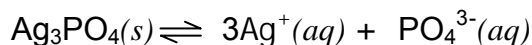
$$x = 4.7 \times 10^{-6} \text{ M} = \text{molar solubility of Ag}_3\text{PO}_4 \text{ in pure water}$$

- b) Calculate the molar solubility of  $\text{Ag}_3\text{PO}_4$  in a solution containing 0.020 M  $\text{Na}_3\text{PO}_4$  (a soluble salt).



Phosphate is the common ion:

$$[\text{PO}_4^{3-}] = [\text{Na}_3\text{PO}_4] = 0.020 \text{ M (since 1 mol Na}_3\text{PO}_4 \text{ forms 1 mol PO}_4^{3-} \text{ ions)}$$



I		0	0.020
C		3x	x
E		3x	0.020+x

$$K_{\text{sp}} = [\text{Ag}^+]^3[\text{PO}_4^{3-}]$$

$$1.3 \times 10^{-20} = (3x)^3 (0.020)$$

$$6.5 \times 10^{-19} = 27x^3$$

$$x^3 = 2.4 \times 10^{-20}$$

$$x = 2.9 \times 10^{-7} \text{ M} = \text{molar solubility of Ag}_3\text{PO}_4 \text{ with a common ion}$$

⇒ Adding common ion decreases the solubility of  $\text{Ag}_3\text{PO}_4$

3. Does AgCl precipitate from a solution containing  $1.0 \times 10^{-5} \text{ M Cl}^-$  and  $1.5 \times 10^{-4} \text{ M Ag}^+$ ?  
 $K_{sp} = 1.8 \times 10^{-10}$

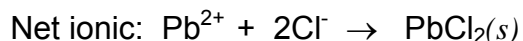
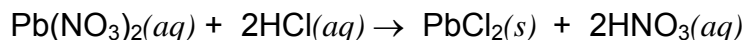
Calculate Q for  $\text{AgCl}(s) \rightleftharpoons \text{Ag}^+ + \text{Cl}^-$

$$Q = [\text{Ag}^+][\text{Cl}^-] = [1.5 \times 10^{-4}][1.0 \times 10^{-5}] = 1.5 \times 10^{-9}$$

$$1.5 \times 10^{-9} > 1.8 \times 10^{-10}; \quad Q > K_{sp}$$

Equilibrium shifts left & solid forms; **AgCl precipitates**

4. If you mix 10.0 ml of 0.0010 M  $\text{Pb}(\text{NO}_3)_2$  with 5.0 ml of 0.015 M HCl, does  $\text{PbCl}_2$  precipitate?  
 $K_{sp}$  of  $\text{PbCl}_2 = 1.6 \times 10^{-5}$



Solubility reaction:  $\text{PbCl}_2(s) \rightleftharpoons \text{Pb}^{2+} + 2\text{Cl}^-$

Calculate Q for  $\text{PbCl}_2$ :  $Q = [\text{Pb}^{2+}][\text{Cl}^-]^2$

$$[\text{Pb}^{2+}] = 0.0010 \text{ M Pb}^{2+} \left( \frac{10.0 \text{ ml}}{10.0 \text{ ml} + 5.0 \text{ ml}} \right) = 6.7 \times 10^{-4} \text{ M Pb}^{2+}$$

$$[\text{Cl}^-] = 0.015 \text{ M Cl}^- \left( \frac{5.0 \text{ ml}}{5.0 \text{ ml} + 10.0 \text{ ml}} \right) = 5.0 \times 10^{-3} \text{ M Cl}^-$$

$$Q = (6.7 \times 10^{-4})(5.0 \times 10^{-3})^2 = 1.7 \times 10^{-8}$$

**$Q < K_{sp}$ , so  $\text{PbCl}_2$  does not precipitate.**