

# 17 Additional Aspects of Aqueous Equilibria

## Visualizing Concepts

- 17.2 (a) According to Figure 16.7, methyl orange is yellow above pH 4.5 and red (really pink) below pH 3.5. The beaker on the left has a pH greater than 4.5, and the one on the right has pH less than 3.5. (By calculation, pH of left beaker = 4.7, pH of right beaker = 2.9.) The right beaker, with lower pH and greater  $[H^+]$ , is pure acetic acid. The left beaker contains equal amounts of the weak acid and its conjugate base, acetic acid and acetate ion. Adding the "common-ion" acetate (in the form of sodium acetate) shifts the acid ionization equilibrium to the left, decreases  $[H^+]$ , and raises pH.
- (b) When small amounts of NaOH are added, the left beaker is better able to maintain its pH. For solutions of the same weak acid, pH depends on the ratio of conjugate base to conjugate acid. Small additions of base (or acid) have the least effect when this ratio is close to one. The left beaker is a buffer because it contains a weak conjugate acid-conjugate base pair and resists rapid pH change upon addition of small amounts of strong base or acid.
- 17.4 *Analyze/Plan.* Consider the reaction  $HA + OH^- \rightarrow A^- + H_2O$ . What are the major species present in solution at the listed stages of the titration? Which diagram represents these species? *Solve.*
- (a) *Before addition of NaOH*, the solution is mostly HA. The only  $A^-$  is produced by the ionization equilibrium of HA and is too small to appear in the diagram. This situation is shown in diagram (iii), which contains only HA.
- (b) *After addition of NaOH but before the equivalence point*, some, but not all, HA has been converted to  $A^-$ . The solution contains a mixture of HA and  $A^-$ ; this is shown in diagram (i).
- (c) *At the equivalence point*, all HA has been converted to  $A^-$ , with no excess HA or  $OH^-$  present. This is shown in diagram (iv).
- (d) *After the equivalence point*, the same amount of  $A^-$  is present as at the equivalence point, plus some excess  $OH^-$ . This is diagram (ii).
- 17.5 *Analyze/Plan.* In each case, the first substance is in the buret, and the second is in the flask. If acid is in the flask, the initial pH is low; with base in the flask, the pH starts high. Strong acids have lower pH than weak acids; strong bases have higher pH than weak bases. Polyprotic acids and bases have more than one "jump" in pH.

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## Solutions to Black Exercises

- (a) Strong base in flask, pH starts high, ends low as acid is added. Only diagram (ii) fits this description.
- (b) Weak acid in flask, pH starts low, but not extremely low. Diagrams (i), (iii), and (iv) all start at low pH and get higher. Diagram (i) has very low initial pH, and likely has strong acid in the flask. Diagram (iv) has two pH jumps, so it has a polyprotic acid in the flask. Diagram (iii) best fits the profile of adding a strong base to a weak acid.
- (c) Strong acid in the flask, pH starts very low, diagram (i).
- (d) Polyprotic acid, more than one pH jump, diagram (iv).
- 17.7 *Analyze/Plan.* Common anions or cations decrease the solubility of salts. Ions that participate in acid-base or complex ion equilibria increase solubility. *Solve.*
- (a)  $\text{CO}_3^{2-}$  from  $\text{BaCO}_3$  reacts with  $\text{H}^+$  from  $\text{HNO}_3$ , causing solubility of  $\text{BaCO}_3$  to increase with increasing  $\text{HNO}_3$  concentration. This behavior matches the right diagram.
- (b) Extra  $\text{CO}_3^{2-}$  from  $\text{Na}_2\text{CO}_3$  decreases the solubility of  $\text{BaCO}_3$ . Solubility of  $\text{BaCO}_3$  decreases as  $[\text{Na}_2\text{CO}_3]$  increases. This behavior matches the left diagram.
- (c)  $\text{NaNO}_3$  has no common ions, nor does it enter into acid-base or complex ion equilibria with  $\text{Ba}^{2+}$  or  $\text{CO}_3^{2-}$ ; it does not affect the solubility of  $\text{BaCO}_3$ . This behavior is shown in the center diagram.
- 17.8 A metal hydroxide that is soluble at very low and very high pH's, that is, in strong acid or strong base, is called amphoteric.

### Common-Ion Effect

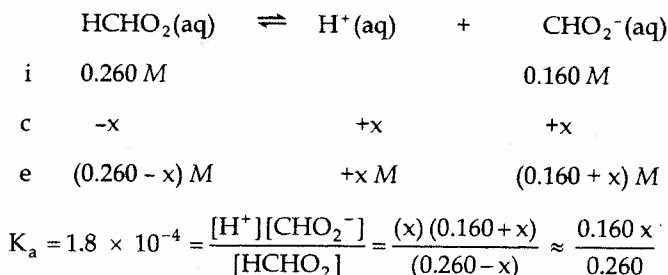
- 17.10 (a) For a generic weak base B,  $K_b = \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B}]}$ . If an external source of  $\text{BH}^+$  such as  $\text{BH}^+\text{Cl}^-$  is added to a solution of  $\text{B}(\text{aq})$ ,  $[\text{BH}^+]$  increases, decreasing  $[\text{OH}^-]$  and increasing  $[\text{B}]$ , effectively suppressing the ionization (hydrolysis) of B.
- (b)  $\text{NH}_4\text{Cl}$
- 17.12 In general, when an acid is added to a solution pH decreases; when a base is added to a solution, pH increases.
- (a) pH increases;  $\text{C}_7\text{H}_5\text{O}_2^-$  decreases ionization of  $\text{HC}_7\text{H}_5\text{O}_2$  and decreases  $[\text{H}^+]$ .
- (b) pH decreases;  $\text{C}_5\text{H}_5\text{NH}^+$  decreases ionization (hydrolysis) of  $\text{C}_5\text{H}_5\text{N}$  and decreases  $[\text{OH}^-]$ .
- (c) pH increases;  $\text{NH}_3$  reacts with  $\text{HCl}$ , decreasing  $[\text{H}^+]$ .
- (d) pH increases;  $\text{HCO}_3^-$  decreases ionization of  $\text{H}_2\text{CO}_3$  and decreases  $[\text{H}^+]$ .
- (e) no change;  $\text{ClO}_4^-$  is a negligible base and  $\text{Na}^+$  is a negligible acid.

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## Solutions to Black Exercises

17.14 *Analyze/Plan.* Follow the logic in Sample Exercise 17.1. *Solve.*

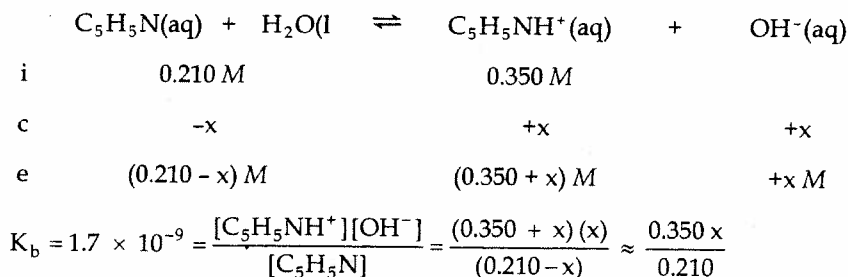
- (a)  $\text{HCHO}_2$  is a weak acid, and  $\text{NaCHO}_2$  contains the common ion  $\text{CHO}_2^-$ , the conjugate base of  $\text{HCHO}_2$ . Solve the common-ion equilibrium problem.



$$x = 2.93 \times 10^{-4} = 2.9 \times 10^{-4}\text{ M} = [\text{H}^+], \text{pH} = 3.53$$

*Check.* Since the extent of ionization of a weak acid or base is suppressed by the presence of a conjugate salt, the 5% rule usually holds true in buffer solutions.

- (b)  $\text{C}_5\text{H}_5\text{N}$  is a weak base, and  $\text{C}_5\text{H}_5\text{NHCl}$  contains the common ion  $\text{C}_5\text{H}_5\text{NH}^+$ , which is the conjugate acid of  $\text{C}_5\text{H}_5\text{N}$ . Solve the common ion equilibrium problem.

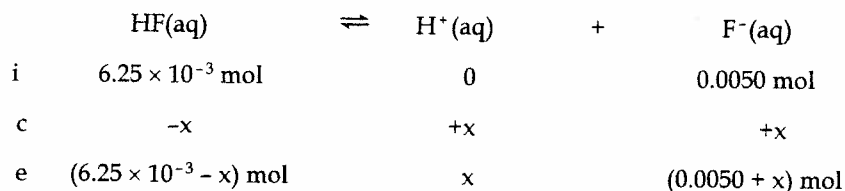


$$x = 1.02 \times 10^{-9} = 1.0 \times 10^{-9}\text{ M} = [\text{OH}^-], \text{pOH} = 8.991, \text{pH} = 14.00 - 8.991 = 5.01$$

*Check.* In a buffer, if [conj. acid] > [conj. base],  $\text{pH} < \text{pK}_a$  of the conj. acid.

If [conj. acid] < [conj. base],  $\text{pH} > \text{pK}_a$  of the conj. acid. In this buffer,  $\text{pK}_a$  of  $(\text{CH}_3)_3\text{NH}^+$  is 9.81.  $[(\text{CH}_3)_3\text{NH}^+] > [(\text{CH}_3)_3\text{N}]$  and  $\text{pH} = 9.61$ , less than 9.81.

- (c)  $\text{mol} = \text{M} \times \text{L}$ ;  $\text{mol HF} = 0.050\text{ M} \times 0.125\text{ L} = 6.25 \times 10^{-3} = 6.3 \times 10^{-3}\text{ mol}$ ;  
 $\text{mol F}^- = 0.10\text{ M} \times 0.0500\text{ L} = 0.0050\text{ mol}$



$$[\text{HF}] = (6.25 \times 10^{-3} + x)/0.175\text{ L}; [\text{F}^-] = (0.0050 + x)/0.175\text{ L}$$

Note that the volumes will cancel when substituted into the  $K_a$  expression.

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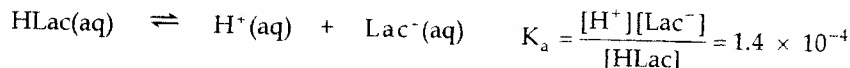
## Solutions to Black Exercises

$$K_a = 6.8 \times 10^{-4} = \frac{[H^+][F^-]}{[HF]} = \frac{x(0.0050+x)/0.175}{(6.25x-x)/0.175} \approx \frac{x(0.0050)}{0.00625}$$

$$x = 8.50 \times 10^{-4} = 8.5 \times 10^{-4} M H^+; pH = 3.07$$

Check.  $pK_a$  for HF = 3.17.  $[HF] > [F^-]$ , pH of buffer = 3.07, less than 3.17.

17.16



$$\text{equil (a)} \quad 0.085 - x M \quad x M \quad x M$$

$$\text{equil (b)} \quad 0.085 - x M \quad x M \quad 0.050 + x M$$

$$(a) \quad K_a = 1.4 \times 10^{-4} = \frac{x^2}{0.085 - x} \approx \frac{x^2}{0.085}; x = [H^+] = 3.45 \times 10^{-3} M = 3.5 \times 10^{-3} M H^+$$

$$\% \text{ ionization} = \frac{3.5 \times 10^{-3} M H^+}{0.085 M Lac} \times 100 = 4.1\% \text{ ionization}$$

$$(b) \quad K_a = 1.4 \times 10^{-4} = \frac{(x)(0.050+x)}{0.085-x} \approx \frac{0.050x}{0.085}; x = 2.4 \times 10^{-4} M H^+$$

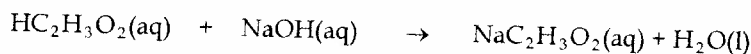
$$\% \text{ ionization} = \frac{2.4 \times 10^{-4} M H^+}{0.085 M Lac} \times 100 = 0.28\% \text{ ionization}$$

### Buffers

17.18 NaOH is a strong base and will react with  $HC_2H_3O_2$  to form  $NaC_2H_3O_2$ . As long as  $HC_2H_3O_2$  is present in excess, the resulting solution will contain both the conjugate acid  $HC_2H_3O_2(aq)$  and the conjugate base  $C_2H_3O_2^-(aq)$ , the requirements for a buffer.

$$\text{mmol} = M \times \text{mL}; \text{mmol } HC_2H_3O_2 = 1.00 M \times 100 \text{ mL} = 10.0 \text{ mmol}$$

$$\text{mmol NaOH} = 0.100 M \times 50 \text{ mL} = 5.0 \text{ mmol}$$



$$\text{initial} \quad 10.0 \text{ mmol} \quad 5.0 \text{ mmol}$$

$$\text{after rx} \quad 5.0 \text{ mmol} \quad 0 \quad 5.0 \text{ mmol}$$

Mixing these two solutions has created a buffer by partial neutralization of the weak acid  $HC_2H_3O_2$ .

17.20 Assume that % ionization is small in these buffers (Solutions 17.15 and 17.16).

(a) The conjugate acid in this buffer is  $HCO_3^-$ , so use  $K_{a2}$  for  $H_2CO_3$ ,  $5.6 \times 10^{-11}$

$$K_a = \frac{[H^+][CO_3^{2-}]}{[HCO_3^-]}; [H^+] = \frac{K_a[HCO_3^-]}{[CO_3^{2-}]} = \frac{5.6 \times 10^{-11} (0.120)}{(0.105)}$$

$$[H^+] = 6.40 \times 10^{-11} = 6.4 \times 10^{-11} M; pH = 10.19$$

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## Solutions to Black Exercises

(b)  $\text{mol} = M \times L$ ; total volume = 140 mL = 0.140 L

$$[\text{H}^+] = \frac{K_a (0.20 \text{ M} \times 0.065 \text{ L}) / 0.120 \text{ L}}{(0.15 \text{ M} \times 0.075 \text{ L}) / 0.120 \text{ L}} = \frac{5.6 \times 10^{-11} (0.20 \times 0.065)}{(0.15 \times 0.075)}$$

$$[\text{H}^+] = 6.47 \times 10^{-11} = 6.5 \times 10^{-11} \text{ M}; \text{pH} = 10.19$$

17.22  $\text{NH}_4^+/\text{NH}_3$  is a basic buffer. Either the hydrolysis of  $\text{NH}_3$  or the dissociation of  $\text{NH}_4^+$  can be used to determine the pH of the buffer. Using the dissociation of  $\text{NH}_4^+$  leads directly to  $[\text{H}^+]$  and facilitates use of the Henderson-Hasselbach relationship.



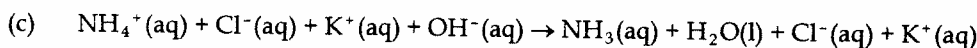
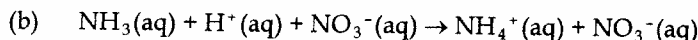
$$K_a = \frac{K_w}{K_b} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

$$[\text{NH}_3] = \frac{5.0 \text{ g NH}_3}{2.50 \text{ L soln}} \times \frac{1 \text{ mol NH}_3}{17.0 \text{ g NH}_3} = 0.118 = 0.12 \text{ M NH}_3$$

$$[\text{NH}_4^+] = \frac{20.0 \text{ g NH}_4\text{Cl}}{2.50 \text{ L}} \times \frac{1 \text{ mol NH}_4\text{Cl}}{53.50 \text{ g NH}_4\text{Cl}} = 0.1495 = 0.15 \text{ M NH}_4^+$$

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]}; [\text{H}^+] = \frac{K_a[\text{NH}_4^+]}{[\text{NH}_3]} = \frac{5.56 \times 10^{-10} (0.1495 - x)}{(0.118 + x)} \approx \frac{5.56 \times 10^{-10} (0.1495)}{(0.118)}$$

$$[\text{H}^+] = 7.044 \times 10^{-10} = 7.0 \times 10^{-10} \text{ M}, \text{pH} = 9.15$$

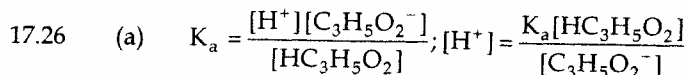


$$[\text{H}^+] = \frac{K_a[\text{HC}_3\text{H}_5\text{O}_3]}{[\text{C}_3\text{H}_5\text{O}_3^-]}; [\text{H}^+] = 10^{-4.00} = 1.0 \times 10^{-4}$$

$$[\text{HC}_3\text{H}_5\text{O}_3] = 0.150 \text{ M}; \text{calculate } [\text{C}_3\text{H}_5\text{O}_3^-]$$

$$[\text{C}_3\text{H}_5\text{O}_3^-] = \frac{K_a[\text{HC}_3\text{H}_5\text{O}_3]}{[\text{H}^+]} = \frac{1.4 \times 10^{-4} (0.150)}{1.0 \times 10^{-4}} = 0.2100 = 0.21 \text{ M}$$

$$\frac{0.210 \text{ mol NaC}_3\text{H}_5\text{O}_3}{1.00 \text{ L}} \times \frac{112.1 \text{ g NaC}_3\text{H}_5\text{O}_3}{1 \text{ mol NaC}_3\text{H}_5\text{O}_3} = 23.54 = 24 \text{ g NaC}_3\text{H}_5\text{O}_3$$

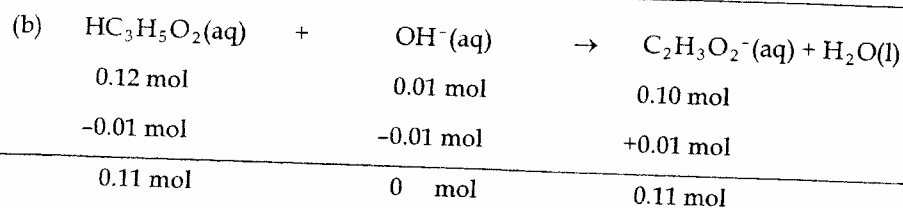


Since this expression contains a ratio of concentrations, we can ignore total volume and work directly with moles.

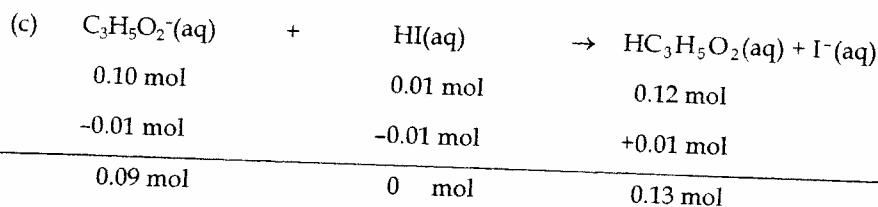
$$[\text{H}^+] = \frac{1.3 \times 10^{-5} (0.12 - x)}{(0.10 + x)} \approx \frac{1.3 \times 10^{-5} (0.12)}{0.10} = 1.56 \times 10^{-5} = 1.6 \times 10^{-5} \text{ M}, \text{pH} = 4.81$$

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## Solutions to Black Exercises



$$[\text{H}^+] \approx \frac{1.3 \times 10^{-5} (0.11)}{(0.11)} = 1.3 \times 10^{-5} \text{ M}; \text{pH} = 4.89$$



$$[\text{H}^+] \approx \frac{1.3 \times 10^{-5} (0.13)}{(0.09)} = 1.88 \times 10^{-3} = 2 \times 10^{-3} \text{ M}; \text{pH} = 4.73 = 4.7$$

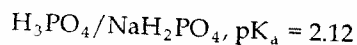
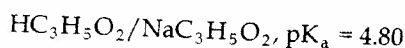
$$17.28 \quad \frac{6.5 \text{ g NaH}_2\text{PO}_4}{0.355 \text{ L soln}} \times \frac{1 \text{ mol NaH}_2\text{PO}_4}{120 \text{ g NaH}_2\text{PO}_4} = 0.153 = 0.15 \text{ M}$$

$$\frac{8.0 \text{ g Na}_2\text{HPO}_4}{0.355 \text{ L soln}} \times \frac{1 \text{ mol Na}_2\text{HPO}_4}{142 \text{ g Na}_2\text{HPO}_4} = 0.159 = 0.16 \text{ M}$$

Use Equation [17.9] to find the pH of the buffer.  $K_a$  for  $\text{H}_2\text{PO}_4^-$  is  $K_{a2}$  for  $\text{H}_3\text{PO}_4$ ,  $6.2 \times 10^{-8}$

$$\text{pH} = -\log(6.2 \times 10^{-8}) + \log \frac{0.159}{0.153} = 7.2076 + 0.0167 = 7.22$$

17.30 The solutes listed contain three possible conjugate acid/conjugate base (CA/CB) pairs. These are:



For maximum buffer capacity,  $\text{p}K_a$  should be within 1 pH unit of the buffer. The propionic acid/propionate pair are most appropriate for a buffer with pH 4.80.

$$\text{pH} = \text{p}K_a + \log \frac{[\text{CB}]}{[\text{CA}]}; 4.80 = 4.886 + \log \frac{[\text{NaC}_3\text{H}_5\text{O}_2]}{[\text{HC}_3\text{H}_5\text{O}_2]}$$

$$\log \frac{[\text{NaC}_3\text{H}_5\text{O}_2]}{[\text{HC}_3\text{H}_5\text{O}_2]} = -0.0861; \frac{[\text{NaC}_3\text{H}_5\text{O}_2]}{[\text{HC}_3\text{H}_5\text{O}_2]} = 0.8202 = 0.82$$

Since we are making a total of 1 L of buffer, let  $y = \text{vol NaC}_3\text{H}_5\text{O}_2$  and  $(1 - y) = \text{vol HC}_3\text{H}_5\text{O}_2$ .

$$0.8202 = \frac{[\text{NaC}_3\text{H}_5\text{O}_2]}{[\text{HC}_3\text{H}_5\text{O}_2]} = \frac{(0.1 \text{ M} \times y)/1.0 \text{ L}}{[0.10 \text{ M} \times (1 - y)]/1.0 \text{ L}} = \frac{0.10 y}{0.10 - 0.10 y}$$

$$0.8202(0.10 - 0.10 y) = 0.10 y; 0.08202 = 0.18202 y; y = 0.4506 = 0.45 \text{ L}$$

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## Solutions to Black Exercises

450 mL of 0.10 M  $\text{NaC}_3\text{H}_5\text{O}_2$ , 550 mL  $\text{HC}_3\text{H}_5\text{O}_2$

Check.  $\text{pH}(\text{buffer}) < \text{pK}_a(\text{CA})$  and the calculated amount of CA in the buffer is greater than the amount of CB.

### Acid-Base Titrations

- 17.32 (a) The quantity of base required to reach the equivalence point is the same in the two titrations.  
 (b) The pH is higher initially in the titration of a weak acid.  
 (c) The pH is higher at the equivalence point in the titration of a weak acid.  
 (d) The pH in excess base is essentially the same for the two cases.  
 (e) In titrating a weak acid, one needs an indicator that changes at a higher pH than for the strong acid titration. The choice is more critical because the change in pH close to the equivalence point is smaller for the weak acid titration.
- 17.34 (a)  $\text{HCHO}_2(\text{aq}) + \text{NaOH}(\text{aq}) \rightarrow \text{NaCHO}_2(\text{aq}) + \text{H}_2\text{O}(\text{l})$   
 At the equivalence point, the major species are  $\text{Na}^+$  and  $\text{CHO}_2^-$ .  $\text{Na}^+$  is negligible and  $\text{CHO}_2^-$  is the CB of  $\text{HCHO}_2$ . The solution is basic, above pH 7.  
 (b)  $\text{Ca}(\text{OH})_2(\text{aq}) + 2\text{HClO}_4(\text{aq}) \rightarrow \text{Ca}(\text{ClO}_4)_2(\text{aq}) + 2\text{H}_2\text{O}(\text{l})$   
 At the equivalence point, the major species are  $\text{Ca}^{2+}$  and  $\text{ClO}_4^-$ ; both are negligible. The solution is at pH 7.  
 (c)  $\text{C}_5\text{H}_5\text{N}(\text{aq}) + \text{HNO}_3(\text{aq}) \rightarrow \text{C}_5\text{H}_5\text{NH}^+\text{NO}_3^-(\text{aq})$   
 At the equivalence point, the major species are  $\text{C}_5\text{H}_5\text{NH}^+$  and  $\text{NO}_3^-$ .  $\text{NO}_3^-$  is negligible and  $\text{C}_5\text{H}_5\text{NH}^+$  is the CA of  $\text{C}_5\text{H}_5\text{N}$ . The solution is acidic, below pH 7.
- 17.36 (a) At the equivalence point, moles HX added = moles B initially present =  $0.10 \text{ M} \times 0.0300 \text{ L} = 0.0030$  moles HX added.  
 (b)  $\text{BH}^+(\text{aq})$   
 (c) Both  $K_a$  for  $\text{BH}^+$  and concentration  $\text{BH}^+$  determine pH at the equivalence point.  
 (d) Because the pH at the equivalence point will be less than 7, methyl red would be more appropriate.
- 17.38 (a)  $55.0 \text{ mL NaOH} \times \frac{0.0950 \text{ mol NaOH}}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}}$   
 $= 49.8 \text{ mL HCl soln}$   
 (b)  $22.5 \text{ mL NH}_3 \times \frac{0.118 \text{ mol NH}_3}{1000 \text{ mL soln}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NH}_3} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}}$   
 $= 25.3 \text{ mL HCl soln}$   
 (c)  $125.0 \text{ mL} \times \frac{1.35 \text{ g NaOH}}{1000 \text{ mL}} \times \frac{1 \text{ mol NaOH}}{40.00 \text{ g NaOH}} \times \frac{1 \text{ mol HCl}}{1 \text{ mol NaOH}} \times \frac{1000 \text{ mL soln}}{0.105 \text{ mol HCl}}$   
 $= 40.2 \text{ mL HCl soln}$

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## Solutions to Black Exercises

17.40 moles  $\text{OH}^- = M_{\text{KOH}} \times L_{\text{KOH}} = 0.150 \text{ M} \times 0.0300 \text{ L} = 4.50 \times 10^{-3} \text{ mol}$

moles  $\text{H}^+ = M_{\text{HClO}_4} \times L_{\text{HClO}_4} = 0.125 \text{ M} \times L_{\text{HClO}_4}$

	mL <sub>KOH</sub>	mL <sub>HClO<sub>4</sub></sub>	Total Volume	Moles OH <sup>-</sup>	Moles H <sup>+</sup>	Molarity Excess Ion	pH
(a)	30.0	30.0	60.0	$4.50 \times 10^{-3}$	$3.75 \times 10^{-3}$	0.0125(OH <sup>-</sup> )	12.10
(b)	30.0	35.0	65.0	$4.50 \times 10^{-3}$	$4.38 \times 10^{-3}$	$1.9 \times 10^{-3}$ (OH <sup>-</sup> )	11.28
(c)	30.0	36.0	66.0	$4.50 \times 10^{-3}$	$4.50 \times 10^{-3}$	$1.0 \times 10^{-7}$ (OH <sup>-</sup> )	7.00
(d)	30.0	37.0	67.0	$4.50 \times 10^{-3}$	$4.63 \times 10^{-3}$	$1.9 \times 10^{-3}$ (H <sup>+</sup> )	2.73
(e)	30.0	40.0	70.0	$4.50 \times 10^{-3}$	$5.00 \times 10^{-3}$	$7.1 \times 10^{-3}$ (H <sup>+</sup> )	2.15

$$\text{molarity of excess ion} = \frac{\text{moles ion}}{\text{total vol in L}}$$

(a)  $\frac{4.50 \times 10^{-3} \text{ mol OH}^- - 3.75 \times 10^{-3} \text{ mol H}^+}{0.0600 \text{ L}} = 0.0125 = 0.013 \text{ M OH}^-$

(b)  $\frac{4.50 \times 10^{-3} \text{ mol OH}^- - 4.38 \times 10^{-3} \text{ mol H}^+}{0.0650 \text{ L}} = 1.92 \times 10^{-3} = 1.9 \times 10^{-3} \text{ M OH}^-$

(c) equivalence point,  $\text{mol H}^+ = \text{mol OH}^-$  M  
 $\text{KClO}_4$  does not hydrolyze, so  $[\text{H}^+] = [\text{OH}^-] = 1 \times 10^{-7}$

(d)  $\frac{4.50 \times 10^{-3} \text{ mol OH}^- - 4.63 \times 10^{-3} \text{ mol H}^+}{0.0670 \text{ L}} = 1.87 \times 10^{-3} = 1.9 \times 10^{-3} \text{ M H}^+$

(e)  $\frac{4.50 \times 10^{-3} \text{ mol OH}^- - 5.00 \times 10^{-3} \text{ mol H}^+}{0.0700 \text{ L}} = 7.14 \times 10^{-3} = 7.1 \times 10^{-3} \text{ M H}^+$

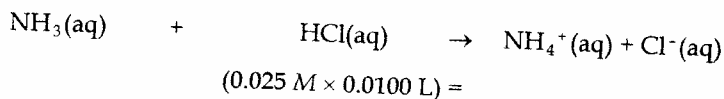
17.42 (a) Weak base problem:  $K_b = 1.8 \times 10^{-5} = \frac{[\text{NH}_4^+][\text{OH}^-]}{[\text{NH}_3]}$

At equilibrium,  $[\text{OH}^-] = x$ ,  $[\text{NH}_3] = (0.030 - x)$ ;  $[\text{NH}_4^+] = x$

$1.8 \times 10^{-5} = \frac{x^2}{(0.030 - x)} \approx \frac{x^2}{0.030}$ ;  $x = [\text{OH}^-] = 7.348 \times 10^{-4} = 7.3 \times 10^{-4} \text{ M}$

$\text{pH} = 14.00 - 3.13 = 10.87$

(b-f) Calculate mol  $\text{NH}_3$  and mol  $\text{NH}_4^+$  after the acid-base reaction takes place.  $0.030 \text{ M NH}_3 \times 0.0300 \text{ L} = 9.0 \times 10^{-4} \text{ mol NH}_3$  present initially.



(b)	before rx	$9.0 \times 10^{-4} \text{ mol}$	$2.5 \times 10^{-4} \text{ mol}$	0 mol
	after rx	$6.5 \times 10^{-4} \text{ mol}$	0 mol	$2.5 \times 10^{-4} \text{ mol}$



# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Black Exercises

		$\text{NH}_3(\text{aq})$	+	$\text{HCl}(\text{aq})$	$\rightarrow$	$\text{NH}_4^+(\text{aq}) + \text{Cl}^-(\text{aq})$
				$(0.025 \text{ M} \times 0.0200 \text{ L}) =$		
(c)	before rx	$9.0 \times 10^{-4} \text{ mol}$		$5.0 \times 10^{-4} \text{ mol}$		0 mol
	after rx	$4.0 \times 10^{-4} \text{ mol}$		0 mol		$5.0 \times 10^{-4} \text{ mol}$
				$(0.025 \text{ M} \times 0.0350 \text{ L}) =$		
(d)	before rx	$9.0 \times 10^{-4} \text{ mol}$		$8.75 \times 10^{-4} \text{ mol}$		0 mol
	after rx	$0.25 \times 10^{-4} \text{ mol}$		0 mol		$8.75 \times 10^{-4} \text{ mol}$
				$(0.025 \text{ M} \times 0.0360 \text{ L}) =$		
(e)	before rx	$9.0 \times 10^{-4} \text{ mol}$		$9.0 \times 10^{-4} \text{ mol}$		0 mol
	after rx	0 mol		0 mol		$9.0 \times 10^{-4} \text{ mol}$
				$(0.025 \text{ M} \times 0.0370 \text{ L}) =$		
(f)	before rx	$9.0 \times 10^{-4} \text{ mol}$		$9.25 \times 10^{-4} \text{ mol}$		0 mol
	after rx	0 mol		$0.25 \times 10^{-4} \text{ mol}$		$9.0 \times 10^{-4} \text{ mol}$

- (b) Using the acid dissociation equilibrium for  $\text{NH}_4^+$  (so that we calculate  $[\text{H}^+]$  directly),  $\text{NH}_4^+(\text{aq}) \rightleftharpoons \text{H}^+(\text{aq}) + \text{NH}_3(\text{aq})$

$$K_a = \frac{[\text{H}^+][\text{NH}_3]}{[\text{NH}_4^+]} = \frac{K_w}{K_b \text{ for } \text{NH}_3} = \frac{1.0 \times 10^{-14}}{1.8 \times 10^{-5}} = 5.56 \times 10^{-10} = 5.6 \times 10^{-10}$$

$$[\text{NH}_3] = \frac{6.5 \times 10^{-4} \text{ mol}}{0.0400 \text{ L}} = 0.01625 \text{ M}; [\text{NH}_4^+] = \frac{2.50 \times 10^{-4} \text{ mol}}{0.0400 \text{ L}} = 6.25 \times 10^{-3} \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} [\text{NH}_4^+]}{[\text{NH}_3]} \approx \frac{5.56 \times 10^{-10} (6.25 \times 10^{-3})}{(0.01625)} = 2.14 \times 10^{-10}; \text{pH} = 9.67$$

(We will assume  $[\text{H}^+]$  is small compared to  $[\text{NH}_3]$  and  $[\text{NH}_4^+]$ .)

$$(c) [\text{NH}_3] = \frac{4.0 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 0.0080 \text{ M}; [\text{NH}_4^+] = \frac{5.0 \times 10^{-4} \text{ mol}}{0.0500 \text{ L}} = 0.010 \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} (0.010)}{(0.0080)} = 6.94 \times 10^{-10} = 6.9 \times 10^{-10} \text{ M}; \text{pH} = 9.16$$

$$(d) [\text{NH}_3] = \frac{0.25 \times 10^{-4} \text{ mol}}{0.0650 \text{ L}} = 3.846 \times 10^{-4} = 4 \times 10^{-4} \text{ M}; [\text{NH}_4^+] = \frac{8.75 \times 10^{-4} \text{ mol}}{0.0650 \text{ L}}$$

$$= 0.01346 = 0.013 \text{ M}$$

$$[\text{H}^+] = \frac{5.56 \times 10^{-10} (0.01346)}{3.846 \times 10^{-4}} = 1.946 \times 10^{-8} = 2 \times 10^{-8} \text{ M}; \text{pH} = 7.7$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Black Exercises

- (e) At the equivalence point,  $[\text{H}^+] = [\text{NH}_3] = x$

$$[\text{NH}_4^+] = \frac{9.0 \times 10^{-4} \text{ M}}{0.0660 \text{ L}} = 0.01364 = 0.014 \text{ M}$$

$$5.56 \times 10^{-10} = \frac{x^2}{0.01364}; x = [\text{H}^+] = 2.754 \times 10^{-6} = 2.8 \times 10^{-6}; \text{pH} = 5.56$$

- (f) Past the equivalence point,  $[\text{H}^+]$  from the excess HCl determines the pH.

$$[\text{H}^+] = \frac{0.25 \times 10^{-4} \text{ mol}}{0.0670 \text{ L}} = 3.731 \times 10^{-4} = 4 \times 10^{-4} \text{ M}; \text{pH} = 3.4$$

- 17.44 The volume of NaOH solution required in all cases is

$$V_{\text{base}} = \frac{V_{\text{acid}} \times M_{\text{acid}}}{M_{\text{base}}} = \frac{(0.100) V_{\text{acid}}}{(0.080)} = 1.25 V_{\text{acid}}$$

The total volume at the equivalence point is  $V_{\text{base}} + V_{\text{acid}} = 2.25 V_{\text{acid}}$ .

The concentration of the salt at the equivalence point is  $\frac{M_{\text{acid}} V_{\text{acid}}}{2.25 V_{\text{acid}}} = \frac{0.100}{2.25} = 0.0444 \text{ M}$

- (a)  $0.0444 \text{ M NaBr}$ ,  $\text{pH} = 7.00$

- (b)  $0.0444 \text{ M Na}^+ \text{C}_3\text{H}_5\text{O}_3^-$ ;  $\text{C}_3\text{H}_5\text{O}_3^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HC}_3\text{H}_5\text{O}_3(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{HC}_3\text{H}_5\text{O}_3][\text{OH}^-]}{[\text{C}_3\text{H}_5\text{O}_3^-]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{1.4 \times 10^{-4}} = 7.14 \times 10^{-11} = 7.1 \times 10^{-11}$$

$$[\text{HC}_3\text{H}_5\text{O}_3] = [\text{OH}^-]; [\text{C}_3\text{H}_5\text{O}_3^-] \approx 0.0444$$

$$[\text{OH}^-]^2 \approx 0.0444(7.14 \times 10^{-11}); [\text{OH}^-] = 1.78 \times 10^{-6} = 1.8 \times 10^{-6} \text{ M}, \text{pOH} = 5.75;$$

$$\text{pH} = 8.25$$

- (c)  $\text{CrO}_4^{2-}(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HCrO}_4^-(\text{aq}) + \text{OH}^-(\text{aq})$

$$K_b = \frac{[\text{HCrO}_4^-][\text{OH}^-]}{[\text{CrO}_4^{2-}]} = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{3.0 \times 10^{-7}} = 3.33 \times 10^{-8} = 3.3 \times 10^{-8}$$

$$[\text{OH}^-]^2 \approx 0.0444(3.33 \times 10^{-8}); [\text{OH}^-] = 3.849 \times 10^{-5} = 3.8 \times 10^{-5}, \text{pH} = 9.59$$

## Solubility Equilibria and Factors Affecting Solubility

- 17.46 (a) Solubility is the amount (grams, moles) of solute that will dissolve in a certain volume of solution. Solubility-product constant is an equilibrium constant, the product of the molar concentrations of all the dissolved ions in solution.

- (b)  $K_{sp} = [\text{Mn}^{2+}][\text{CO}_3^{2-}]; K_{sp} = [\text{Hg}^{2+}][\text{OH}^-]^2; K_{sp} = [\text{Cu}^{2+}]^3[\text{PO}_4^{3-}]^2$

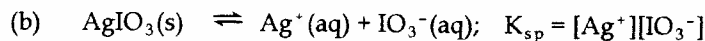
- 17.48 (a)  $\text{PbBr}_2(\text{s}) \rightleftharpoons \text{Pb}^{2+}(\text{aq}) + 2\text{Br}^-(\text{aq})$

$$K_{sp} = [\text{Pb}^{2+}][\text{Br}^-]^2; [\text{Pb}^{2+}] = 1.0 \times 10^{-2} \text{ M}, [\text{Br}^-] = 2.0 \times 10^{-2} \text{ M}$$

$$K_{sp} = (1.0 \times 10^{-2} \text{ M})(2.0 \times 10^{-2} \text{ M})^2 = 4.0 \times 10^{-6}$$

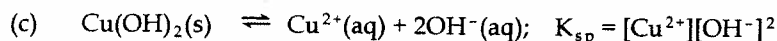
# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Black Exercises



$$[\text{Ag}^+] = [\text{IO}_3^-] = \frac{0.0490 \text{ g AgIO}_3}{1.00 \text{ L soln}} \times \frac{1 \text{ mol AgIO}_3}{282.8 \text{ g AgIO}_3} = 1.733 \times 10^{-4} = 1.73 \times 10^{-4} \text{ M}$$

$$K_{\text{sp}} = (1.733 \times 10^{-4} \text{ M})(1.733 \times 10^{-4} \text{ M}) = 3.00 \times 10^{-8}$$



$$[\text{Cu}^{2+}] = x, [\text{OH}^-] = 2x; K_{\text{sp}} = 4.8 \times 10^{-20} = (x)(2x)^2$$

$$4.8 \times 10^{-20} = 4x^3; x = [\text{Cu}^{2+}] = 2.290 \times 10^{-7} = 2.3 \times 10^{-7} \text{ M}$$

$$\frac{2.290 \times 10^{-7} \text{ mol Cu}(\text{OH})_2}{1 \text{ L}} \times \frac{97.56 \text{ g Cu}(\text{OH})_2}{1 \text{ mol Cu}(\text{OH})_2} = 2.2 \times 10^{-5} \text{ g Cu}(\text{OH})_2$$

However,  $[\text{OH}^-]$  from  $\text{Cu}(\text{OH})_2 = 4.58 \times 10^{-7} \text{ M}$ ; this is similar to  $[\text{OH}^-]$  from the autoionization of water.

$$K_{\text{w}} = [\text{H}^+][\text{OH}^-]; [\text{H}^+] = y, [\text{OH}^-] = (4.58 \times 10^{-7} + y)$$

$$1.0 \times 10^{-14} = y(4.58 \times 10^{-7} + y); y^2 + 4.58 \times 10^{-7}y - 1.0 \times 10^{-14}$$

$$y = \frac{-4.58 \times 10^{-7} \pm \sqrt{(4.58 \times 10^{-7})^2 - 4(1)(-1.0 \times 10^{-14})}}{2}; y = 2.09 \times 10^{-8}$$

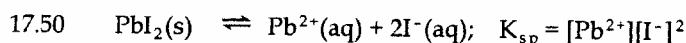
$$[\text{OH}^-]_{\text{total}} = 4.58 \times 10^{-7} \text{ M} + 0.209 \times 10^{-7} \text{ M} = 4.79 \times 10^{-7} \text{ M}$$

Recalculating  $[\text{Cu}^{2+}]$  and thus molar solubility of  $\text{Cu}(\text{OH})_2(\text{s})$ :

$$4.8 \times 10^{-20} = x(4.79 \times 10^{-7})^2; x = 2.09 \times 10^{-7} \text{ M Cu}^{2+}$$

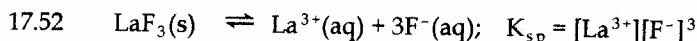
$$\frac{2.09 \times 10^{-7} \text{ mol Cu}(\text{OH})_2(\text{s})}{1 \text{ L}} \times \frac{97.56 \text{ g Cu}(\text{OH})_2}{1 \text{ mol Cu}(\text{OH})_2} = 2.0 \times 10^{-5} \text{ g Cu}(\text{OH})_2$$

Note that the presence of  $\text{OH}^-$  as a common ion decreases the water solubility of  $\text{Cu}(\text{OH})_2$ .



$$[\text{Pb}^{2+}] = \frac{0.54 \text{ g PbI}_2}{1.00 \text{ L soln}} \times \frac{1 \text{ mol PbI}_2}{461.0 \text{ g PbI}_2} = 1.17 \times 10^{-3} = 1.2 \times 10^{-3} \text{ M}$$

$$[\text{I}^-] = 2[\text{Pb}^{2+}]; K_{\text{sp}} = [\text{Pb}^{2+}](2[\text{Pb}^{2+}])^2 = 4[\text{Pb}^{2+}]^3 = 4(1.17 \times 10^{-3})^3 = 6.4 \times 10^{-9}$$



(a) molar solubility =  $x = [\text{La}^{3+}]; [\text{F}^-] = 3x$

$$K_{\text{sp}} = 2 \times 10^{-19} (x)(3x)^3; 2 \times 10^{-19} = 27x^4; x = (7.41 \times 10^{-21})^{1/4}, x = 9.28 \times 10^{-6} \\ = 9 \times 10^{-6} \text{ M La}^{3+}$$

$$\frac{9.28 \times 10^{-6} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 1.82 \times 10^{-3} = 2 \times 10^{-3} \text{ g LaF}_3/\text{L}$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Black Exercises

- (b) molar solubility =  $x = [\text{La}^{3+}]$

There are two sources of  $\text{F}^-$ :  $\text{KF}(0.010 \text{ M})$  and  $\text{LaF}_3(3x \text{ M})$

$$K_{\text{sp}} = (x)(0.010 + 3x)^3; \text{ assume } x \text{ is small compared to } 0.010 \text{ M.}$$

$$2 \times 10^{-16} = (0.010)^3 x; x = 2 \times 10^{-16} / 1.0 \times 10^{-6} = 2 \times 10^{-13} \text{ M La}^{3+}$$

$$\frac{2 \times 10^{-13} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 3.92 \times 10^{-11} = 4 \times 10^{-11} \text{ g LaF}_3 / \text{L}$$

- (c) molar solubility =  $x$ ,  $[\text{F}^-] = 3x$ ,  $[\text{La}^{3+}] = 0.050 \text{ M} + x$

$$K_{\text{sp}} = (0.050 + x)(3x)^3; \text{ assume } x \text{ is small compared to } 0.050 \text{ M.}$$

$$2 \times 10^{-19} = (0.050)(27x^3) = 1.35x^3; x = (1.48 \times 10^{-19})^{1/3} = 5.29 \times 10^{-7} = 5 \times 10^{-7} \text{ M}$$

$$\frac{5.29 \times 10^{-7} \text{ mol LaF}_3}{1 \text{ L}} \times \frac{195.9 \text{ g LaF}_3}{1 \text{ mol}} = 1.04 \times 10^{-4} = 1 \times 10^{-4} \text{ g LaF}_3 / \text{L}$$

- 17.54  $\text{Fe}(\text{OH})_2(\text{s}) \rightleftharpoons \text{Fe}^{2+}(\text{aq}) + 2\text{OH}^-(\text{aq}); K_{\text{sp}} = 8.0 \times 10^{-16}$

Since the  $[\text{OH}^-]$  is set by the pH of the solution, the solubility of  $\text{Fe}(\text{OH})_2$  is just  $[\text{Fe}^{2+}]$ .

- (a)  $\text{pH} = 7.0$ ,  $\text{pOH} = 14 - \text{pH} = 7.0$ ,  $[\text{OH}^-] = 10^{-\text{pOH}} = 1.0 \times 10^{-7} = 1 \times 10^{-7} \text{ M}$

$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}](1.0 \times 10^{-7})^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-14}} = 7.9 \times 10^{-2} = 8 \times 10^{-2} \text{ M}$$

Check. In pure water,  $[\text{OH}^-]$  from  $\text{Fe}(\text{OH})_2$  is similar to  $(\text{OH}^-)$  from the autoionization of water, resulting in a cubic equation for  $[\text{Fe}^{2+}]$ . The solubility of  $\text{Fe}(\text{OH})_2$  at a buffered  $\text{pH} = 7.0$  is actually greater than the solubility in pure water.

- (b)  $\text{pH} = 10.0$ ,  $\text{pOH} = 4.0$ ,  $[\text{OH}^-] = 1.0 \times 10^{-4} = 1 \times 10^{-4} \text{ M}$

$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}][1.0 \times 10^{-4}]^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-8}} = 7.9 \times 10^{-8} = 8 \times 10^{-8} \text{ M}$$

- (c)  $\text{pH} = 12.0$ ,  $\text{pOH} = 2.0$ ,  $[\text{OH}^-] = 1.0 \times 10^{-2} = 1 \times 10^{-2} \text{ M}$

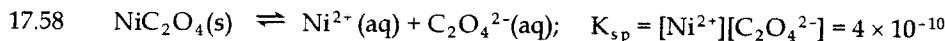
$$K_{\text{sp}} = 7.9 \times 10^{-16} = [\text{Fe}^{2+}][1.0 \times 10^{-2}]^2; [\text{Fe}^{2+}] = \frac{7.9 \times 10^{-16}}{1.0 \times 10^{-4}} = 7.9 \times 10^{-12} = 8 \times 10^{-12} \text{ M}$$

- 17.56 If the anion in the slightly soluble salt is the conjugate base of a strong acid, there will be no reaction.

- (a)  $\text{MnS}(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{S}(\text{aq}) + \text{Mn}^{2+}(\text{aq})$   
 (b)  $\text{PbF}_2(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow 2\text{HF}(\text{aq}) + \text{Pb}^{2+}(\text{aq})$   
 (c)  $\text{AuCl}_3(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{no reaction}$   
 (d)  $\text{Hg}_2\text{C}_2\text{O}_4(\text{s}) + 2\text{H}^+(\text{aq}) \rightarrow \text{H}_2\text{C}_2\text{O}_4(\text{aq}) + \text{Hg}_2^{2+}(\text{aq})$   
 (e)  $\text{CuBr}(\text{s}) + \text{H}^+(\text{aq}) \rightarrow \text{no reaction}$

# 17 Additional Aspects of Aqueous Equilibria

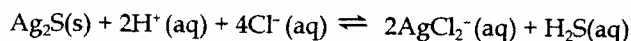
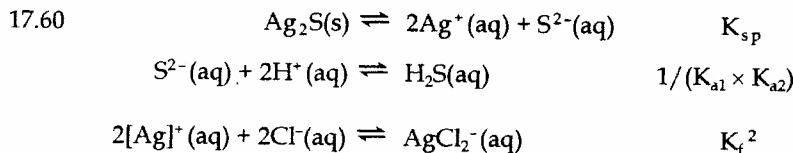
## Solutions to Black Exercises



When the salt has just dissolved,  $[\text{C}_2\text{O}_4^{2-}]$  will be 0.020 M. Thus  $[\text{Ni}^{2+}]$  must be less than  $4 \times 10^{-10} / 0.020 = 2 \times 10^{-8}$  M. To achieve this low  $[\text{Ni}^{2+}]$  we must complex the  $\text{Ni}^{2+}$  ion with  $\text{NH}_3$ :  $\text{Ni}^{2+}(\text{aq}) + 6\text{NH}_3(\text{aq}) \rightleftharpoons \text{Ni}(\text{NH}_3)_6^{2+}(\text{aq})$ . Essentially all  $\text{Ni}(\text{II})$  is in the form of the complex, so  $[\text{Ni}(\text{NH}_3)_6^{2+}] = 0.020$ . Find  $K_f$  for  $\text{Ni}(\text{NH}_3)_6^{2+}$  in Table 17.1.

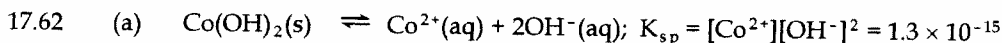
$$K_f = \frac{[\text{Ni}(\text{NH}_3)_6^{2+}]}{[\text{Ni}^{2+}][\text{NH}_3]^6} = \frac{(0.020)}{(2 \times 10^{-8})(\text{NH}_3)^6} = 1.2 \times 10^9; [\text{NH}_3]^6 = 8.33 \times 10^{-4};$$

$$[\text{NH}_3] = 0.307 = 0.3 \text{ M}$$



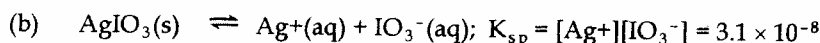
$$K = \frac{K_{\text{sp}} \times K_f^2}{K_{\text{a1}} \times K_{\text{a2}}} = \frac{(6 \times 10^{-51})(1.1 \times 10^5)^2}{(9.5 \times 10^{-8})(1 \times 10^{-19})} = 7.64 \times 10^{-15} = 8 \times 10^{-15}$$

### Precipitation; Qualitative Analysis



$$\text{pH} = 8.5; \text{pOH} = 14 - 8.5 = 5.5; [\text{OH}^-] = 10^{-5.5} = 3.16 \times 10^{-6} = 3 \times 10^{-6} \text{ M}$$

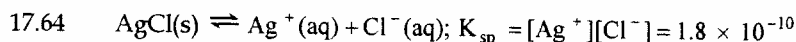
$$Q = (0.020)(3.16 \times 10^{-6})^2 = 2 \times 10^{-13}; Q > K_{\text{sp}}, \text{Co}(\text{OH})_2 \text{ will precipitate}$$



$$[\text{Ag}^+] = \frac{0.010 \text{ M Ag}^+ \times 0.100 \text{ L}}{0.110 \text{ L}} = 9.09 \times 10^{-3} = 9.1 \times 10^{-3} \text{ M}$$

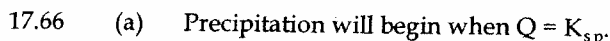
$$[\text{IO}_3^-] = \frac{0.015 \text{ M IO}_3^- \times 0.010 \text{ L}}{0.110 \text{ L}} = 1.36 \times 10^{-3} = 1.4 \times 10^{-3} \text{ M}$$

$$Q = (9.09 \times 10^{-3})(1.36 \times 10^{-3}) = 1.2 \times 10^{-5}; Q > K_{\text{sp}}, \text{AgIO}_3 \text{ will precipitate}$$



$$[\text{Ag}^+] = \frac{0.10 \text{ M} \times 0.2 \text{ mL}}{10 \text{ mL}} = 2 \times 10^{-3} \text{ M}; [\text{Cl}^-] = \frac{1.8 \times 10^{-10}}{2 \times 10^{-3} \text{ M}} = 9 \times 10^{-8} \text{ M}$$

$$\frac{9 \times 10^{-8} \text{ mol Cl}^-}{1 \text{ L}} \times \frac{35.45 \text{ g Cl}^-}{1 \text{ mol Cl}^-} \times 0.010 \text{ L} = 3.19 \times 10^{-8} \text{ g Cl}^- = 3 \times 10^{-8} \text{ g Cl}^-$$

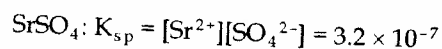


$$\text{BaSO}_4: K_{\text{sp}} = [\text{Ba}^{2+}][\text{SO}_4^{2-}] = 1.1 \times 10^{-10}$$

$$1.1 \times 10^{-10} = (0.010)[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 1.1 \times 10^{-8} \text{ M}$$

# 17 Additional Aspects of Aqueous Equilibria

## Solutions to Black Exercises



$$3.2 \times 10^{-7} = (0.010)[\text{SO}_4^{2-}]; [\text{SO}_4^{2-}] = 3.2 \times 10^{-5} M$$

The  $[\text{SO}_4^{2-}]$  necessary to begin precipitation is the smaller of the two values,  $1.1 \times 10^{-8} M \text{SO}_4^{2-}$ .

- (b)  $\text{Ba}^{2+}$  precipitates first, because it requires the smaller  $[\text{SO}_4^{2-}]$ .
- (c)  $\text{Sr}^{2+}$  will begin to precipitate when  $[\text{SO}_4^{2-}]$  in solution (not bound in  $\text{BaSO}_4$ ) reaches  $3.2 \times 10^{-5} M$ .
- 17.68 Initial solubility in water rules out  $\text{CdS}$  and  $\text{HgO}$ . Formation of a precipitate on addition of  $\text{HCl}$  indicates the presence of  $\text{Pb}(\text{NO}_3)_2$  (formation of  $\text{PbCl}_2$ ). Formation of a precipitate on addition of  $\text{H}_2\text{S}$  at pH 1 probably indicates  $\text{Cd}(\text{NO}_3)_2$  (formation of  $\text{CdS}$ ). (This test can be misleading because enough  $\text{Pb}^{2+}$  can remain in solution after filtering  $\text{PbCl}_2$  to lead to visible precipitation of  $\text{PbS}$ .) Absence of a precipitate on addition of  $\text{H}_2\text{S}$  at pH 8 indicates that  $\text{ZnSO}_4$  is not present. The yellow flame test indicates presence of  $\text{Na}^+$ . In summary,  $\text{Pb}(\text{NO}_3)_2$  and  $\text{Na}_2\text{SO}_4$  are definitely present,  $\text{Cd}(\text{NO}_3)_2$  is probably present, and  $\text{CdS}$ ,  $\text{HgO}$  and  $\text{ZnSO}_4$  are definitely absent.
- 17.70 (a) Make the solution slightly basic and saturate with  $\text{H}_2\text{S}$ ;  $\text{CdS}$  will precipitate,  $\text{Na}^+$  remains in solution.
- (b) Make the solution acidic, saturate with  $\text{H}_2\text{S}$ ;  $\text{CuS}$  will precipitate,  $\text{Mg}^{2+}$  remains in solution.
- (c) Add  $\text{HCl}$ ,  $\text{PbCl}_2$  precipitates. (It is best to carry out the reaction in an ice-water bath to reduce the solubility of  $\text{PbCl}_2$ .)
- (d) Add dilute  $\text{HCl}$ ;  $\text{AgCl}$  precipitates,  $\text{Hg}^{2+}$  remains in solution.
- 17.72 The addition of  $(\text{NH}_4)_2\text{HPO}_4$  could result in precipitation of salts from metal ions of the other groups. The  $(\text{NH}_4)_2\text{HPO}_4$  will render the solution basic, so metal hydroxides could form as well as insoluble phosphates. It is essential to separate the metal ions of a group from other metal ions before carrying out the specific tests for that group.

### Additional Exercises

17.74  $K_a = \frac{[\text{H}^+][\text{In}^-]}{[\text{HIn}]}$ ; at pH = 4.68,  $[\text{HIn}] = [\text{In}^-]$ ;  $[\text{H}^+] = K_a$ ; pH =  $\text{p}K_a = 4.68$

- 17.75 (a)  $\text{HA}(\text{aq}) + \text{B}(\text{aq}) \rightleftharpoons \text{HB}^+(\text{aq}) + \text{A}^-(\text{aq})$   $K_{eq} = \frac{[\text{HB}^+][\text{A}^-]}{[\text{HA}][\text{B}]}$
- (b) Note that the solution is slightly basic because B is a stronger base than HA is an acid. (Or, equivalently, that  $\text{A}^-$  is a stronger base than  $\text{HB}^+$  is an acid.) Thus, a little of the  $\text{A}^-$  is used up in reaction:  $\text{A}^-(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{HA}(\text{aq}) + \text{OH}^-(\text{aq})$ . Since pH is not very far from neutral, it is reasonable to assume that the reaction in part (a) has gone far to the right, and that  $[\text{A}^-] \approx [\text{HB}^+]$  and  $[\text{HA}] \approx [\text{B}]$ . Then