

- 84 The pK_a of the indicator methyl orange is 3.46. Over what pH range does this indicator change from 90 percent HIn to 90 percent In^- ?

We can use the Henderson-Hasselbalch equation to solve for the pH when the indicator is 90% acid / 10% conjugate base and when the indicator is 10% acid / 90% conjugate base.

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}$$

Solving for the pH with 90% of the indicator in the HIn form:

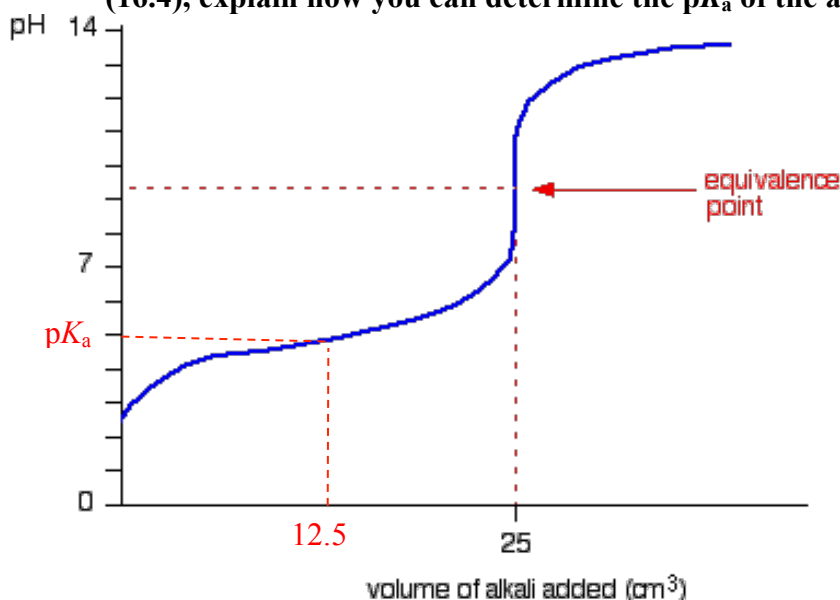
$$pH = 3.46 + \log \frac{[10]}{[90]} = 3.46 - 0.95 = 2.51$$

Next, solving for the pH with 90% of the indicator in the In^- form:

$$pH = 3.46 + \log \frac{[90]}{[10]} = 3.46 + 0.95 = 4.41$$

Thus the pH range varies from 2.51 to 4.41 as the [HIn] varies from 90% to 10%.

- 85 Sketch the titration curve of a weak acid versus a strong base like the one shown in Figure 16.5. On your graph indicate the volume of base used at the equivalence point and also at the half-equivalence point, that is, the point at which half of the acid has been neutralized. Show how you can measure the pH of the solution at the half-equivalence point. Using Equation (16.4), explain how you can determine the pK_a of the acid by this procedure.



To measure the pH at the half-equivalence point, titrate with $\frac{1}{2}$ the needed amount of alkali (OH^-)—in this case, 12.5 mL, or back-titrate with 12.5 mL of strong acid such as HCl, then use a pH probe to measure the pH.

Referring to Figure 16.5, at the half-equivalence point, $[\text{weak acid}] = [\text{conjugate base}]$. Using the Henderson-Hasselbalch equation:

$$pH = pK_a + \log \frac{[\text{conjugate base}]}{[\text{acid}]}, \text{ so } pH = pK_a$$

- 87 The pK_a of butyric acid (HBut) is 4.7. Calculate K_b for the butyrate ion (But^-)

The K_a of butyric acid is obtained by setting $K_a = 10^{-pK_a} = 10^{-4.7} = 2 \times 10^{-5}$. The value of K_b is:

$$K_b = \frac{K_w}{K_a} = \frac{1.0 \times 10^{-14}}{2 \times 10^{-5}} = 5 \times 10^{-10}$$

- 88** A solution is made by mixing exactly 500 mL of 0.167 M NaOH with exactly 500 mL 0.100 M HCOOH. Calculate the equilibrium concentrations of H^+ , HCOOH, $HCOO^-$, and Na^+ .

The resulting solution is not a buffer system. There is excess NaOH and the neutralization is well past the equivalence point. *The only equilibrium, therefore, is from the hydrolysis of $HCOO^-$ to form HCOOH.*

$$\text{Moles NaOH} = 0.500 \text{ L} \times \frac{0.167 \text{ mol}}{1 \text{ L}} = 0.0835 \text{ mol}$$

$$\text{Moles HCOOH} = 0.500 \text{ L} \times \frac{0.100 \text{ mol}}{1 \text{ L}} = 0.0500 \text{ mol}$$

	$HCOOH(aq) + NaOH(aq) \rightarrow HCOONa(aq) + H_2O(l)$		
Initial (mol):	0.0500	0.0835	0
Change (mol):	-0.0500	-0.0500	+0.0500
Final (mol):	0	0.0335	0.0500

The volume of the resulting solution is 1.00 L (500 mL + 500 mL = 1000 mL).

$$[OH^-] = \frac{0.0335 \text{ mol}}{1.00 \text{ L}} = \mathbf{0.0335 \text{ M}}$$

$$[Na^+] = \frac{(0.0335 + 0.0500) \text{ mol}}{1.00 \text{ L}} = \mathbf{0.0835 \text{ M}}$$

$$[H^+] = \frac{K_w}{[OH^-]} = \frac{1.0 \times 10^{-14}}{0.0335} = \mathbf{3.0 \times 10^{-13} \text{ M}}$$

$$[HCOO^-] = \frac{0.0500 \text{ mol}}{1.00 \text{ L}} = \mathbf{0.0500 \text{ M}}$$

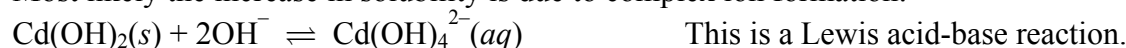
	$HCOO^-(aq) + H_2O(l) \rightleftharpoons HCOOH(aq) + OH^-(aq)$		
Initial (M):	0.0500	0	0.0335
Change (M):	-x	+x	+x
Equilibrium (M):	$0.0500 - x$	x	$0.0335 + x$

$$K_b = \frac{[HCOOH][OH^-]}{[HCOO^-]} = \frac{(x)(0.0335 + x)}{(0.0500 - x)} \approx \frac{(x)(0.0335)}{(0.0500)} = 5.9 \times 10^{-11}$$

$$x = [HCOOH] = \mathbf{8.8 \times 10^{-11} \text{ M}}$$

- 89** $Cd(OH)_2$ is an insoluble compound. It dissolves in excess NaOH in solution. Write a balanced ionic equation for this reaction. What type of reaction is this?

Most likely the increase in solubility is due to complex ion formation:



- 94** Calculate the solubility (in g/L) of Ag_2CO_3 .

First we find the molar solubility and then convert moles to grams. The solubility equilibrium for silver carbonate is:

	$Ag_2CO_3(s) \rightleftharpoons 2Ag^+(aq) + CO_3^{2-}(aq)$		
Initial (M):	0	0	
Change (M):	-s	+2s	+s
Equilibrium (M):	2s	s	

$$K_{sp} = [\text{Ag}^+]^2[\text{CO}_3^{2-}] = (2s)^2(s) = 4s^3 = 8.1 \times 10^{-12}; s = \left(\frac{8.1 \times 10^{-12}}{4}\right)^{1/3} = 1.3 \times 10^{-4} M$$

Converting from mol/L to g/L:

$$\frac{1.3 \times 10^{-4} \text{ mol}}{1 \text{ L soln}} \times \frac{275.8 \text{ g}}{1 \text{ mol}} = \mathbf{0.036 \text{ g/L}}$$

- 95 Find the approximate pH range suitable for separating Mg^{2+} and Zn^{2+} by the precipitation of $\text{Zn}(\text{OH})_2$ from a solution that is initially $0.010 M$ in Mg^{2+} and Zn^{2+} .**

For $\text{Mg}(\text{OH})_2$, $K_{sp} = 1.2 \times 10^{-11}$. When $[\text{Mg}^{2+}] = 0.010 M$, the $[\text{OH}^-]$ value is

$$K_{sp} = [\text{Mg}^{2+}][\text{OH}^-]^2 \quad \text{or} \quad [\text{OH}^-] = \left(\frac{K_{sp}}{[\text{Mg}^{2+}]}\right)^{1/2} = \left(\frac{1.2 \times 10^{-11}}{0.010}\right)^{1/2} = 3.4 \times 10^{-5} M$$

This $[\text{OH}^-]$ corresponds to a pH of 9.54. $\text{Mg}(\text{OH})_2$ will begin to precipitate from this solution at pH of 9.54.

For $\text{Zn}(\text{OH})_2$, $K_{sp} = 1.8 \times 10^{-14}$. When $[\text{Zn}^{2+}] = 0.010 M$, the $[\text{OH}^-]$ value is

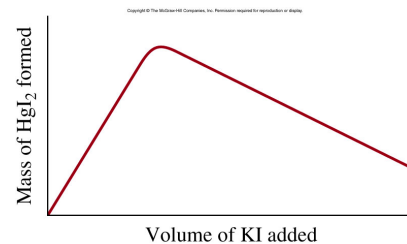
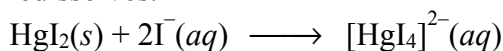
$$[\text{OH}^-] = \left(\frac{K_{sp}}{[\text{Zn}^{2+}]}\right)^{1/2} = \left(\frac{1.8 \times 10^{-14}}{0.010}\right)^{1/2} = 1.3 \times 10^{-6} M$$

This corresponds to a pH of 8.11. In other words $\text{Zn}(\text{OH})_2$ will begin to precipitate from the solution at pH = 8.11. These results show that $\text{Mg}(\text{OH})_2$ will precipitate when the pH just exceeds 9.54 and that $\text{Zn}(\text{OH})_2$ will precipitate when the pH just exceeds 8.11. Therefore, to selectively precipitate $\text{Zn}(\text{OH})_2$, the pH must be greater than 8.11 but less than 9.54.

- 98 When a KI solution was added to a solution of mercury(II) chloride, a precipitate [mercury(II) iodide] formed. A student plotted the mass of the precipitate versus the volume of the KI solution added and obtained the following graph. Explain the appearance of the graph.**

The precipitate is HgI_2 : $\text{Hg}^{2+}(\text{aq}) + 2\text{I}^-(\text{aq}) \longrightarrow \text{HgI}_2(\text{s})$

With further addition of I^- , a soluble complex ion is formed and the precipitate redissolves.



- 101 Solid NaBr is slowly added to a solution that is $0.010 M$ in Cu^+ and $0.010 M$ in Ag^+ .**

(a) Which compound will begin to precipitate first?

The solubility product expressions for both substances *have exactly the same mathematical form* and are therefore *directly comparable*. The substance having the smaller K_{sp} (**AgBr**) will precipitate first. (Why?)

(b) Calculate $[\text{Ag}^+]$ when CuBr just begins to precipitate.

When CuBr just begins to precipitate the solubility product expression will just equal K_{sp} (saturated solution). The concentration of Cu^+ at this point is 0.010 M (given in the problem), so the concentration of bromide ion must be:

$$K_{\text{sp}} = [\text{Cu}^+][\text{Br}^-] = (0.010)[\text{Br}^-] = 4.2 \times 10^{-8}$$

$$[\text{Br}^-] = \frac{4.2 \times 10^{-8}}{0.010} = 4.2 \times 10^{-6}\text{ M}$$

$$\text{so, } [\text{Ag}^+] = \frac{K_{\text{sp}}}{[\text{Br}^-]} = \frac{7.7 \times 10^{-13}}{4.2 \times 10^{-6}} = 1.8 \times 10^{-7}\text{ M}$$

(c) What percent of Ag^+ remains in solution at this point?

The percent of silver ion remaining in solution is:

$$\% \text{Ag}^+(\text{aq}) = \frac{1.8 \times 10^{-7}\text{ M}}{0.010\text{ M}} \times 100\% = 0.0018\% \text{ or } 1.8 \times 10^{-3}\%$$

Is this an effective way to separate silver from copper?