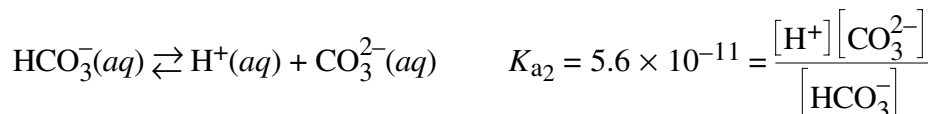
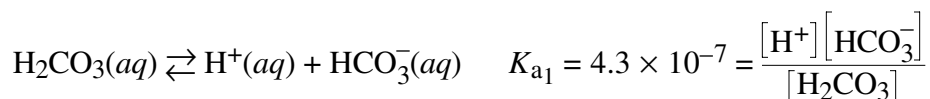


Problem Set 5 Solutions (For February 10)

1. We look up the K_a values in Table 7.4 right off the bat, and write them down with the equilibria they represent:



Both of these equilibrium constants are small, meaning each step is a characteristic “weak acid” scenario. We begin with the analytic concentration of carbonic acid: $[\text{H}_2\text{CO}_3]_0 = 0.034 \text{ M}$. We expect this to be close to the equilibrium concentration because K_{a1} is small for H_2CO_3 . This means $[\text{H}^+] = [\text{HCO}_3^-] = x$ and we write, invoking the usual weak base approximation,

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{[\text{H}_2\text{CO}_3] - x} \approx \frac{x^2}{[\text{H}_2\text{CO}_3]} = \frac{x^2}{0.034}$$

or, solving for x , $x = [\text{H}^+] = 1.2 \times 10^{-4} \text{ M}$ or $\text{pH} = 3.92$. Note that $[\text{H}^+] \ll [\text{H}_2\text{CO}_3]_0$ as we anticipated. We find $[\text{CO}_3^{2-}]$ easily from the second dissociation equilibrium:

$$K_{a2} = 5.6 \times 10^{-11} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{x[\text{CO}_3^{2-}]}{x} = [\text{CO}_3^{2-}]$$

which shows us the interesting result that for a pure diprotic acid solution, the concentration of the final species in the dissociation chain equals the equilibrium constant for the reaction that produces it. Now, we move to $\text{pH} = 10.0$. We should stop a minute and think: what are the dominant species in the solution at this pH ? Picture (or better yet, make a sketch of) the titration curve for our initial solution. It starts at $\text{pH} = 3.92$, the value we calculated above. Then, half way to the first equivalence point, the pH rises to $\text{p}K_{a1} = 6.37$. At the first equivalence point, we have shown that the pH is given by the average of the two $\text{p}K$ values for the steps on either side of this point:

$$\text{pH} = \frac{\text{p}K_{a1} + \text{p}K_{a2}}{2} = \frac{[-\log(4.3 \times 10^{-7})] + [-\log(5.6 \times 10^{-11})]}{2} = \frac{6.37 + 10.25}{2} = 8.31$$

From there, we move into the second stage of the titration (turning HCO_3^- into CO_3^{2-}). Half-way through that second stage, the $\text{pH} = \text{p}K_{a2} = 10.25$. Thus, if we are at $\text{pH} = 10.0$, we’re not quite to the half-equivalence point of the second titration. If we were exactly there, we’d know that $[\text{H}_2\text{CO}_3]$ is very, very small while $[\text{HCO}_3^-] = [\text{CO}_3^{2-}]$. Since we’re a bit shy of that pH , we know that these two species should have comparable concentrations with $[\text{HCO}_3^-]$ a bit larger than $[\text{CO}_3^{2-}]$. We focus on the second stage equilibrium and write, with $x = [\text{CO}_3^{2-}]$ and $[\text{HCO}_3^-] = 0.034 - x$ (because *always* the sum of the three carbon-containing species’ concentrations must add to the 0.034 M analytic concentration *and* we are in a region where the H_2CO_3 concentration is very small),

$$K_{a2} = 5.6 \times 10^{-11} = \frac{[\text{H}^+][\text{CO}_3^{2-}]}{[\text{HCO}_3^-]} = \frac{(10^{-10})x}{0.034 - x}$$

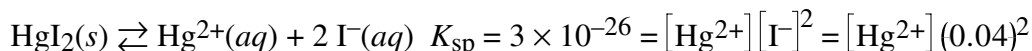
$$\text{or } x = [\text{CO}_3^{2-}] = 0.0122 \text{ M} \quad \text{and} \quad [\text{HCO}_3^-] = 0.034 - x = 0.0218 \text{ M}$$

Then we find $[\text{H}_2\text{CO}_3]$:

$$K_{a1} = 4.3 \times 10^{-7} = \frac{[\text{H}^+][\text{HCO}_3^-]}{[\text{H}_2\text{CO}_3]} = \frac{(10^{-10})(0.0218)}{[\text{H}_2\text{CO}_3]} \quad \text{so that} \quad [\text{H}_2\text{CO}_3] = 5.07 \times 10^{-6} \text{ M}$$

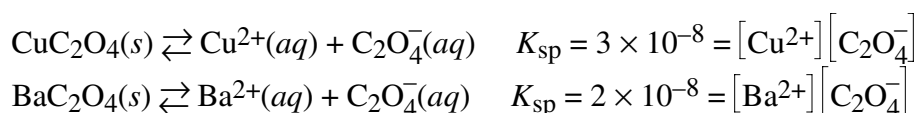
Problem Set 5 Solutions (For February 10)

2. In 20.0 mL of 0.10 M $\text{Hg}(\text{NO}_3)_2$, we have $(0.020 \text{ L})(0.10 \text{ M}) = 2 \text{ mmol Hg}^{2+}$ and twice this amount, 4 mmol, of NO_3^- . In 30.0 mL of 0.20 M NaI , we have $(0.030 \text{ L})(0.20 \text{ M}) = 6 \text{ mmol of Na}^+$ and 6 mmol of I^- . If we mix these two volumes, our 50.0 mL final volume, assuming no reaction, has the following concentrations: $[\text{Hg}^{2+}] = (0.002 \text{ mol})/(0.050 \text{ L}) = 0.04 \text{ M}$, $[\text{NO}_3^-] = 0.08 \text{ M}$, $[\text{Na}^+] = (0.006 \text{ mol})/(0.050 \text{ L}) = 0.12 \text{ M} = [\text{I}^-]$. But now we recognize that HgI_2 will precipitate, and we need to determine the limiting reagent. Because each Hg^{2+} that precipitates takes with it two I^- ions, we see that Hg^{2+} is limiting. When it is “all gone” from the solution, it will have taken with it $2 \times (2 \text{ mmol}) = 0.004 \text{ mol}$ of I^- with it, leaving only 0.002 mol behind. This amount establishes $[\text{I}^-] = 0.04 \text{ M}$, and we find the true equilibrium $[\text{Hg}^{2+}]$ from the K_{sp} expression:



or $[\text{Hg}^{2+}] = 1.8 \times 10^{-23} \text{ M}$! There's maybe *one* Hg^{2+} ion in solution!

3. Here, we have to satisfy two *coupled* equilibria, coupled in the sense that both of them have a species, the oxalate ion, in common:



Certainly, some of both compounds will dissolve. Let the equilibrium concentrations of the metal ions be $[\text{Cu}^{2+}] = x$ and $[\text{Ba}^{2+}] = y$. Whenever one Cu^{2+} enters solution, it brings one oxalate with it, and similarly for Ba^{2+} . Thus, the equilibrium oxalate concentration must be $[\text{C}_2\text{O}_4^{2-}] = x + y$.

We now have a “two equations in two unknowns” problem to solve:

$$\begin{aligned} K_{\text{sp}} = 3 \times 10^{-8} &= [\text{Cu}^{2+}][\text{C}_2\text{O}_4^{2-}] = x(x + y) \\ K_{\text{sp}} = 2 \times 10^{-8} &= [\text{Ba}^{2+}][\text{C}_2\text{O}_4^{2-}] = y(x + y) \end{aligned}$$

If we divide the top equation by the bottom one, the $(x + y)$ factors cancel, and we find $x/y = 3/2$, or $x = 3y/2$. Let's substitute this expression for x into the first equation:

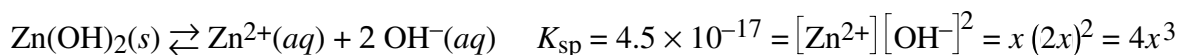
$$K_{\text{sp}} = 3 \times 10^{-8} = [\text{Cu}^{2+}][\text{C}_2\text{O}_4^{2-}] = x(x + y) = \frac{3y}{2} \left(\frac{3y}{2} + y \right) = \left[\left(\frac{3}{2} \right)^2 + \frac{3}{2} \right] y^2$$

Solving this expression for y gives us $y = [\text{Ba}^{2+}] = 8.94 \times 10^{-5} \text{ M}$. We find $x = 3y/2 = [\text{Cu}^{2+}] = 1.34 \times 10^{-4} \text{ M}$, and finally, $[\text{C}_2\text{O}_4^{2-}] = x + y = 2.23 \times 10^{-4}$. Let's check these numbers to be sure they satisfy the equilibrium constant expressions:

$$\begin{aligned} K_{\text{sp}} = 3 \times 10^{-8} &= [\text{Cu}^{2+}][\text{C}_2\text{O}_4^{2-}] = (1.34 \times 10^{-4})(2.23 \times 10^{-4}) = 2.99 \times 10^{-8} \quad (\text{good enough}) \\ K_{\text{sp}} = 2 \times 10^{-8} &= [\text{Ba}^{2+}][\text{C}_2\text{O}_4^{2-}] = (8.94 \times 10^{-5})(2.23 \times 10^{-4}) = 1.99 \times 10^{-8} \quad (\text{good enough}) \end{aligned}$$

To within roundoff error, we're in agreement!

4. Although the problem didn't ask us to do this explicitly, let's consider dissolving $\text{Zn}(\text{OH})_2$ in pure water first. The equilibrium and K_{sp} expression here is (in direct analogy to the CaF_2 solubility we discussed in class)



and we find $x = [\text{Zn}^{2+}] = 2.24 \times 10^{-6} \text{ M}$. Now, in a pH 6.00 buffer, decidedly but not overwhelmingly acidic, we have fixed $[\text{H}^+] = 10^{-6}$ so that $[\text{OH}^-] = 10^{-8}$ (because $[\text{H}^+][\text{OH}^-] = K_{\text{w}} = 10^{-14}$ always). With this value for $[\text{OH}^-]$, we have

Problem Set 5 Solutions (For February 10)

$$K_{\text{sp}} = 4.5 \times 10^{-17} = [\text{Zn}^{2+}][\text{OH}^-]^2 = [\text{Zn}^{2+}](10^{-8})^2 \quad \text{or} \quad [\text{Zn}^{2+}] = \frac{4.5 \times 10^{-17}}{(10^{-8})^2} = 0.45 \text{ M}$$

That's a *huge* increase in solubility! With a molar mass for $\text{Zn}(\text{OH})_2$ of 99.4 g mol^{-1} , we find that in pure water the solubility is only $2.23 \times 10^{-4} \text{ g L}^{-1}$, but in the buffer, it is 44.7 g L^{-1} .

5. We're told that the solution is made by dissolving 0.100 mol of a soluble Fe^{3+} salt in 1.00 L of water. This tells us the analytic concentration $[\text{Fe}^{3+}]_0 = 0.100 \text{ M}$. At equilibrium (where $[\text{H}^+] = 10^{-1.6} \text{ M} = 2.5 \times 10^{-2} \text{ M}$), we must have $[\text{Fe}^{3+}] + [\text{FeOH}^{2+}] = [\text{Fe}^{3+}]_0$. But we also must have $[\text{FeOH}^{2+}] = [\text{H}^+]$, according to the stoichiometry of the net hydrolysis reaction. We write

$$K = \frac{[\text{H}^+][\text{FeOH}^{2+}]}{[\text{Fe}^{3+}]} = \frac{(2.5 \times 10^{-2})(2.5 \times 10^{-2})}{(0.100 - 2.5 \times 10^{-2})} = 8.4 \times 10^{-3}$$

and also find $[\text{FeOH}^{2+}]/[\text{Fe}^{3+}] = K/[\text{H}^+] = 0.335$.