

You must show your work for full credit.

Exp 5 Questions

1. An ammonia buffer is made by adding 15.0 mL of 0.100 M NH_3 solution to 35.0 mL of 0.120 M NH_4Cl . For the following calculations, you can assume that this buffer behaves as a traditional buffer. $K_a(\text{NH}_4^+ \text{ ion}) = 5.6 \times 10^{-10}$.

a) Calculate the pH of this solution. (2 pt)

$\text{pH} = \text{p}K_a + \log([\text{NH}_3]/[\text{NH}_4^+])$ or $= \text{p}K_a + \log[n(\text{NH}_3)/n(\text{NH}_4^+)]$ (moles used so we don't need to recalculate diluted concentrations)

$\text{pH} = -\log(5.6 \times 10^{-10}) + \log[(0.0015 \text{ mol})/(0.0042 \text{ mol})] = 9.25 + \log(0.357) = 9.25 - 0.45 = \mathbf{8.80}$
using 1st equation and dilution, $\text{pH} = 9.25 + \log[(0.0300 \text{ M})/(0.084 \text{ M})] = 9.25 + \log(0.357) = \mathbf{8.80}$

Can also use the K_a equation directly as in lab manual

b) Now 5.0 mL of 0.100 M NaOH is added to the buffer. What is the new pH? Be sure to show the reaction that happens from addition of NaOH. (3 pts)

Added OH^- reacts with the acid form in the reaction shown below. Since the equilibrium constant ($1/K_b$) strongly favors the products, OH^- will be used up converting NH_4^+ to NH_3 . This can be expressed quantitatively by making a mole table (see below), which first requires a calculation of the moles of OH^- added. $\text{Moles}(\text{OH}^-) = (0.0050\text{L})(0.100 \text{ mol/L}) = 0.0005 \text{ mol}$

| | | | |
|-------------|---|---------|---------|
| | $\text{OH}^-(\text{aq}) + \text{NH}_4^+(\text{aq}) \leftrightarrow \text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l})$ | | |
| initially: | 0.0005 | 0.0042 | 0.0015 |
| change: | -0.0005 | -0.0005 | +0.0005 |
| full right: | 0 | 0.0037 | 0.0020 |

Now, the H-H equation can be used: $\text{pH} = \text{p}K_a + \log[n(\text{NH}_3)/n(\text{NH}_4^+)] = 9.25 - 0.54 = \mathbf{8.98}$

c) The original buffer (no addition of NaOH) is diluted to a total of 100.0 mL. What is the new pH? Explain your answer. (1 pt)

$\mathbf{\text{pH} = 8.80}$ (or same answer as in a)). Dilution reduces NH_3 and NH_4^+ by the same factor – the ratio of concentrations stays the same.

Solubility problem

2. Chromate, CrO_4^{2-} , is a toxic form of chromium (in the +6 oxidation state). It is desired to separate CrO_4^{2-} from SO_4^{2-} in a mixture that contains CrO_4^{2-} and SO_4^{2-} at concentrations of 0.080 and 0.020 M, respectively. The K_{sp} values for SrCrO_4 and SrSO_4 are 3.6×10^{-5} and 3.44×10^{-7} , respectively.

a) Which ion will precipitate first as Sr^{2+} is added? (1 pt)

We can calculate $[\text{Sr}^{2+}]$ when each ion first precipitates. $K_{\text{sp}}(\text{SrCrO}_4) = [\text{Sr}^{2+}][\text{CrO}_4^{2-}]$ or solving for $[\text{Sr}^{2+}]$, $[\text{Sr}^{2+}] = 3.6 \times 10^{-5}/[\text{CrO}_4^{2-}] = 4.5 \times 10^{-4} \text{ M}$. For $[\text{SO}_4^{2-}]$, $[\text{SO}_4^{2-}] = 3.44 \times 10^{-7}/0.020 = 1.72 \times 10^{-5} \text{ M}$. Since Sr^{2+} precipitates out at a lower concentration for SO_4^{2-} , $\mathbf{\text{SO}_4^{2-} \text{ precipitates first}}$.

Note: can also compare K_{sp} (not always accurate but reasonable in this case).

(continued on back)

b) Perform calculations to show whether it is possible to isolate CrO_4^{2-} from 99% of the SO_4^{2-} present by Sr^{2+} addition (assume no dilution occurs in the Sr^{2+} addition). (Hint: 99% removal means 1% left). (3 pts)

Having done the calculations in part a), we can use $[\text{Sr}^{2+}]$ at the start of CrO_4^{2-} precipitation to determine the equilibrium $[\text{SO}_4^{2-}]$ left at that Sr^{2+} level. $K_{sp}(\text{SrSO}_4) = [\text{Sr}^{2+}][\text{SO}_4^{2-}]$ or $[\text{SO}_4^{2-}] = 3.44 \times 10^{-7}/4.5 \times 10^{-4} = 7.64 \times 10^{-4} \text{ M}$

Now we can determine what percent of the original SO_4^{2-} is left in the solution that contains the CrO_4^{2-} that we are trying to isolate.

$\% = (7.64 \times 10^{-4} \text{ M}) * 100 / 0.020 = 3.8\%$. In order to meet our separation criteria, we needed to remove 99+% of sulfate and this shows that **it is not possible to isolate chromate at the desired level.**

Note: one can also calculate whether at 1% of original sulfate precipitation, whether chromate would already have started precipitating. $(0.01)(0.020) = 2.0 \times 10^{-4} \text{ M}$ and then Sr^{2+} in equilibrium will have concentration $= K_{sp}(\text{SrSO}_4) / [\text{SO}_4^{2-}] = 1.7 \times 10^{-3}$ or $Q = [\text{Sr}^{2+}][\text{CrO}_4^{2-}] = (1.7 \times 10^{-3})(0.080) = 1.4 \times 10^{-4} > K_{sp}(\text{SrCrO}_4)$. Since $Q > K$, precipitation of chromate would occur before getting to 1% of the initial sulfate.