Mid-Term Examination
CHEM*2400/2480
Summer 2004

# SOLUTIONS

1. Straightforward application of our statistics equations. Bear in mind that n = 7 while degrees of freedom = 6. Be sure to get the right term from the t-table.

$$C.I. = \frac{t\,s}{\sqrt{n}} = \frac{3.707 \times 0.0008\%}{\sqrt{7}} = 0.0011\%$$
$$1.5321 \pm 0.0011\%$$

2. Here we are comparing two sets of data to see if they agree with each other. We must calculate a pooled standard deviation, note that the degrees of freedom are the some of the number of samples – 2, because we have found 2 means from the collective data. We then compare the calculated t to the tabulated t to determine if the two sets of data are saying something different or not.

$$s_{\text{pooled}} = \sqrt{\frac{(0.08_2)^2(5) + (0.06_1)^2(4)}{9}} = 0.07_3$$
$$t_{\text{calculated}} = \frac{|5.27_9 - 5.18_2|}{0.07_3}\sqrt{\frac{6 \times 5}{6 + 5}} = 2.194$$
$$t_{\text{table}}(95\%; n = 9) = 2.262$$
$$t_{\text{calculated}} < t_{\text{table}}$$

The new employee has satisfied the criterion and can work independently now.

3. Here is a solubility problem with a common ion present. The first estimate will be to ignore the oxalate coming from the solvation of the slightly soluble salt, assuming that oxalate concentration will be controlled by the soluble alt present.

$$K_{sp} = [La^{3+}]^2[C_2O_4^{2-}]^3 = 1.02 \times 10^{-25} = (2x)^2(0.0500 + 3x)^3 \approx (2x)^2(0.0500)^3$$
$$x = \sqrt{\frac{1.02 \times 10^{-25}}{4 \times (0.0500)^3}} = 1.43 \times 10^{-11}\,\text{M}$$

4. (a) First find the hydroxide concentration.

$$n(\text{sulfamic acid}) = \frac{0.3155\,\text{g}}{97.095\,\text{g/mol}} = 0.003249\,\text{mol}$$
$$n(\text{NaOH}) = n(\text{sulfamic acid}) = 0.003249\,\text{mol}$$
$$[\text{NaOH}] = \frac{0.003249\,\text{mol}}{0.02891\,\text{L}} = 0.1124\,\text{M}$$

(b) Now find the malonic acid concentration. Note that malonic acid is diprotic, so there is only 1/2 as many moles of malonic acid as there are moles of NaOH.

$$n(\text{NaOH}) = 0.1124\,M \times 0.01421\,L = 0.001597\text{ mol}$$

$$\frac{1}{2} \times n(\text{NaOH}) = n(\text{malonic acid}) = \frac{1}{2} \times 0.001597\text{ mol} = 0.0007986\text{ mol}$$

$$[\text{malonic acid}] = \frac{0.0007986\text{ mol}}{0.1000\text{ L}} = 0.07986\text{ M}$$

5. (a) The stoichiometry between titrant and analyte is 1:1 so the moles of analyte must equal the moles of titrant at the equivalence point.

$$n(Mn^{2+}) = 0.02500\text{ L} \times 0.07150\text{ M} = 0.001787_5\text{ mol}$$

$$V(CO_3^{2-}) = \frac{0.001787_5\text{ mol}}{0.05842\text{ M}} = 0.03060\text{ L} = 30.60\text{ mL}$$

(b) (i) This added volume is before the equivalence point so that the analyte is the species in excess. We solve for its concentration and then use the equilibrium to find the minor species concentration.

$$[\text{Mn}^{2+}] = 0.07150\text{ M}\left(\frac{5.60\text{ mL}}{30.60\text{ mL}}\right)\left(\frac{25.00\text{ mL}}{50.00\text{ mL}}\right) = 0.006542\text{ M}$$

$$[\text{CO}_3^{2-}] = \frac{K_{\text{sp}}}{[\text{Mn}^{2+}]} = \frac{5.02 \times 10^{-10}}{0.006542} = 7.674 \times 10^{-8}\text{ M}$$

$$p(\text{CO}_3^{2-}) = -\log(7.674 \times 10^{-8}) = 7.1150$$

(ii) This is after the equivalence point; the titrant is in excess so we can calculate the carbonate concentration directly.

$$[\text{CO}_3^{2-}] = 0.05842\text{ M}\left(\frac{4.40\text{ mL}}{60.00\text{ mL}}\right) = 0.004284\text{ M}$$

$$p(\text{CO}_3^{2-}) = -\log(0.004284) = 2.3681$$

6. (a) Calculate the concentration of cobalticyanide right when the precipitate will start to form. This is the same as when the salt would dissolve to reach equilibrium. Recall, however, that we have the concentration of the metal ions given already so the calculation is quite straightforward.

$$K_{sp}\left(Ag_3Co(CN)_6^{3-}\right) = [Ag^+]^3\left[Co(CN)_6^{3-}\right] = 3.93 \times 10^{-26}$$

$$\left[Co(CN)_6^{3-}\right]_{Ag^+} = \frac{3.93 \times 10^{-26}}{(0.1000)^3} = 3.93 \times 10^{-23}$$

and for the other ion

$$K_{sp}\left((Hg_2)_3\left(Co(CN)_6^{3-}\right)_2\right) = [Hg_2^{2+}]^3\left[Co(CN)_6^{3-}\right]^2 = 1.94 \times 10^{-37}$$

$$\left[Co(CN)_6^{3-}\right]_{Hg_2^{2+}} = \sqrt{\frac{1.94 \times 10^{-37}}{(0.1000)^3}} = 1.39 \times 10^{-17}$$

The concentration of cobalticyanide in the analyte container begins (obviously) at zero. It rises until its concentration exceeds that needed for precipitation of the first ion. The Ag ion will precipitate first since the concentration needed for its precipitation is smaller than that needed for the mercurous ion.

(b) The first equivalence point will occur when the amount of added cobalticyanide stoichiometrically equals the amount of silver originally present. Note that three Ag ions precipitate with each cobalticyanide.

$$n\left(Ag^{+}\right) = 0.1000\ \text{M} \times 0.02000\ \text{L} = 0.002000\ \text{mol}$$

$$\frac{1}{3}n\left(Ag^{+}\right) = n\left(Co\left(CN\right)_6^{3-}\right) = \frac{1}{3}(0.002000\ \text{mol}) = 0.0006667\ \text{mol}$$

$$V_1\left(Co\left(CN\right)_6^{3-}\right) = \frac{0.0006667\ \text{mol}}{0.1000\ \text{M}} = 0.006667\ \text{L} = 6.67\ \text{mL}$$

(c) This volume is before the first equivalence point. We can calculate the Ag concentration by dilution and reaction and then use the equilibrium to find the cobalticyanide.

$$\left[Ag^{+}\right] = 0.1000\ \text{M} \times \left(\frac{1.67\ \text{mL}}{6.67\ \text{mL}}\right) \times \left(\frac{20.00\ \text{mL}}{25.00\ \text{mL}}\right) = 0.02003\ \text{M}$$

$$\left[Co\left(CN\right)_6^{3-}\right] = \frac{K_{sp}}{\left[Ag^{+}\right]^3} = \frac{3.93 \times 10^{-26}}{(0.02003)^3} = 4.89 \times 10^{-21}\ \text{M}$$

(d) We still need a concentration of $1.39 \times 10^{-17}$ M of cobalticyanide to induce precipitation of the mercurous ion. Therefore, at the concentration of $4.89 \times 10^{-21}$ M, the mercurous ion has still not started to precipitate.

(e) We need to know where the 2nd equivalence point occurs to know if this amount of added titrant exceeds or is before that point. Note that the stoichiometry in this case is that 2/3 as much cobalticyanide is needed than there is mercurous ion present.

$$n\left(Hg_2^{2+}\right) = 0.1000\ \text{M} \times 0.02000\ \text{L} = 0.002000\ \text{mol}$$

$$\frac{2}{3} \times n\left(Hg_2^{2+}\right) = n\left(Co\left(CN\right)_6^{3-}\right) = \frac{2}{3}(0.002000\ \text{mol}) = 0.001333\ \text{mol}$$

$$V_2\left(Co\left(CN\right)_6^{3-}\right) = \frac{0.001333\ \text{mol}}{0.1000\ \text{M}} = 0.01333\ \text{L} = 13.33\ \text{mL}$$

This is the volume need for the titration of the mercurous ion. The second endpoint, however, can only occur after the first – both species must be titrated separately, so the actual endpoint is the sum of the first and second titration volumes, or 6.67 mL + 13.33 mL = 20.00 mL. Therefore, the added volume of 25.00 mL is after the second endpoint and the titrant must now be in excess. We can find the titrant concentration directly by considering dilution and from the two equilibria we can find the concentration of the two metal species.

$$\left[Co\left(CN\right)_6^{3-}\right] = 0.1000\ \text{M} \times \left(\frac{5.00\ \text{mL}}{45.00\ \text{mL}}\right) = 0.01111\ \text{M}$$

$$\left[Ag^{+}\right] = \sqrt[3]{\frac{3.93 \times 10^{-26}}{0.01111}} = 1.52 \times 10^{-8}\ \text{M}$$

$$\left[Hg_2^{2+}\right] = \sqrt[3]{\frac{1.94 \times 10^{-37}}{(0.01111)^2}} = 1.16 \times 10^{-11}\ \text{M}$$