

CHEMISTRY 31 EXAM 2

Nov. 9, 2016

KEY

Some Useful Constants:

$$R = 8.314 \text{ J mol}^{-1} \text{ K}^{-1} \quad 0^\circ\text{C} = 273 \text{ K}$$

$$K_w \text{ (autoprotolysis constant for H}_2\text{O)} = 1.0 \times 10^{-14}$$

$$h = \text{Planck's constant} = 6.63 \times 10^{-34} \text{ J}\cdot\text{s}; \quad c = \text{speed of light} = 3.00 \times 10^8 \text{ m s}^{-1}$$

A. Multiple Choice/Fill in the Blank Section. Only one correct answer for multiple choice questions. (4 points for each question)

1. The cation and anion of an insoluble salt are mixed together. In order to determine if precipitation is likely, the best thing to look at is:

- a) If the value of K_{sp} for the pair is $< 10^{-5}$
- b) If Q (for K_{sp} reaction) exceeds K_{sp}**
- c) If the salt stoichiometry is 2:1 (cation: anion) or higher
- d) There is no way to predict if precipitation is likely

2. In the reaction: $\text{NH}_3(\text{aq}) + \text{H}_2\text{O}(\text{l}) \rightleftharpoons \text{NH}_4^+(\text{aq}) + \text{OH}^-(\text{aq})$, $\text{NH}_4^+(\text{aq})$ can be identified as:

- a) the Lewis base
- b) the conjugate acid**
- c) the conjugate base
- e) the Lewisonium ion

3. Given the weak acids listed in the table and their pK_a values, which base is the strongest?

Acid	HSCN	HF	HONH_3^+	HBO_3
pK_a	0.89	3.17	5.96	9.24

- a) NaSCN
- b) KF
- c) HONH_2
- d) NaBO_3**

$$14 = pK_a + pK_b \text{ so, } pK_b = 14 - pK_a \text{ so largest } pK_a \text{ means conjugate base is strongest}$$

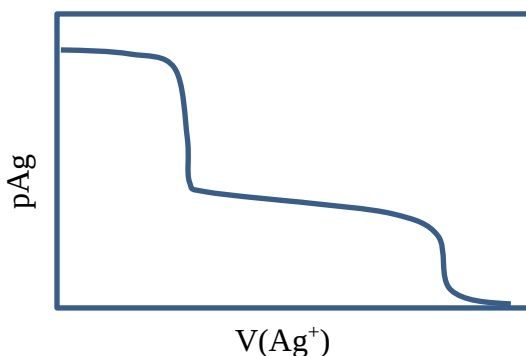
4. Which of the following requirements is needed for a titration to be successful?

- a) the equilibrium constant for the reaction must be large**
- b) reactants must react with 1:1 stoichiometry
- c) a reactant or product must be colored
- d) the titrant needs to be made from a primary standard

5. A mixture of I^- and Cl^- is analyzed by precipitation titration by adding Ag^+ from a buret (K_{sp} for AgI and AgCl are 8.3×10^{-17} and 1.8×10^{-8} , respectively). By looking at the titration plot (to right), we can see that:

- a) Cl^- precipitates out first
- b) The unknown contains more I^- than Cl^-
- c) The unknown contains more Cl^- than I^-**
- d) Neither endpoint is sharp

$K_{sp} \text{ for } \text{AgI} > K_{sp} \text{ for } \text{AgCl}$ so first sharp drop is for I^- . $V(\text{Ag}^+)$ between two drops is larger



6. A standardization titration is most common where:
 a) a titrant is available as a primary standard b) a back titration cannot be used
 c) a titrant cannot be prepared accurately from solids d) no standards of the analyte exist
7. The purpose of a monochromator is to:
 a) detect light transmitted through the sample in a spectrometer
 b) select a single ion in an ion chromatograph
 c) to detect gases leaving a gas chromatograph
 d) to select a single wavelength of light in a spectrometer
8. Absorption of light causing changes in outer shell electron states is caused by:
 a) X-rays b) ultraviolet light c) microwaves d) radio waves
9. In open tubular gas chromatography columns, the stationary phase is most commonly:
 a) a thin coating bonded to the inside of a narrow column
 b) a coating on packing material in a column
 c) the surface of packing material in a column
 d) an organic compound collected from waves off of Hawaii
10. A normal phase HPLC method is used to separate phenols using a mobile phase of 80% hexane and 20% 2-propanol (a polar organic molecule). There is not enough separation to resolve some phenols. In order to increase retention factors, the chemist should:
 a) decrease the temperature b) increase the % 2-propanol
 c) decrease the % 2-propanol d) increase the flow rate
we want a weaker eluent (one less like the stationary phase which is more hexane)

B. Problem Section. Show all needed calculations to receive full credit. The number of points are shown in parentheses. Use the back side of the page if needed.

1. A solution contains chromate, CrO_4^{2-} , at 0.080 M, and chloride at 0.050 M and it is desired to separate the two ions. Both form sparingly soluble salts with Ag^+ . The K_{sp} values for Ag_2CrO_4 and AgCl are 1.12×10^{-12} and 1.77×10^{-10} , respectively.

a) Calculate $[\text{Ag}^+]$ when each anion starts precipitating (2 calculations) and decide which anion precipitates out first. (5 pt)

For $[\text{CrO}_4^{2-}] = 0.080$, $1.12 \times 10^{-12} = [\text{Ag}^+]^2[\text{CrO}_4^{2-}]$ or $[\text{Ag}^+] = (1.12 \times 10^{-12}/0.080)^{0.5}$

$[\text{Ag}^+] = 3.74 \times 10^{-6}$

For $[\text{Cl}^-] = 0.050$, $1.77 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-]$ or $[\text{Ag}^+] = 1.77 \times 10^{-10}/0.050$

$[\text{Ag}^+] = 3.54 \times 10^{-9}$

Since a lower $[\text{Ag}^+]$ occurs with Cl^- , Cl^- precipitates out first

b) Calculate the concentration of the first anion to precipitate when enough Ag^+ has been added so that $[\text{Ag}^+]$ is just high enough to start precipitating the second anion. (5 pts)

This would be when $[\text{Ag}^+] = 3.74 \times 10^{-6}$. $[\text{Cl}^-] = 1.77 \times 10^{-10}/3.74 \times 10^{-6} = 4.73 \times 10^{-5} \text{ M}$

2. Mercury(II) ion (Hg^{2+}) reacts with CH_3CO_2^- in the reaction, $\text{Hg}^{2+} + 2\text{CH}_3\text{CO}_2^- \leftrightarrow \text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})$ forming a complex ion ($K = 2.82 \times 10^8$). Calculate the ratio of Hg(II) in the complexed ($\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})$) to uncomplexed form if CH_3CO_2^- is present at equilibrium at 0.0050 M. (6 pts)

$$K = 2.82 \times 10^8 = [\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})]/[\text{Hg}^{2+}][\text{CH}_3\text{CO}_2^-]^2$$

$$[\text{Hg}(\text{CH}_3\text{CO}_2)_2(\text{aq})]/[\text{Hg}^{2+}] = K[\text{CH}_3\text{CO}_2^-]^2 = (2.82 \times 10^8)(0.0050)^2 = \mathbf{7.0 \times 10^3}$$

3. A 25.0 mL aliquot of a sample containing an unknown concentration of Cl^- is titrated by addition of Ag^+ . It takes 37.11 mL of 0.00800 M Ag^+ to reach an end point. $K_{\text{sp}}(\text{AgCl}) = 1.77 \times 10^{-10}$

a) What is the concentration of Cl^- in the sample. (5 pts)

$$\text{Ag}^+ + \text{Cl}^- \leftrightarrow \text{AgCl}(s) \text{ so } n(\text{Ag}^+) = n(\text{Cl}^-) \text{ or } [\text{Cl}^-]V(\text{Cl}^-) = [\text{Ag}^+]V(\text{Ag}^+)$$

$$[\text{Cl}^-] = (37.11 \text{ mL})(0.00800 \text{ M})/(25.0 \text{ mL}) = \mathbf{0.0119 \text{ M}}$$

b) What is $[\text{Ag}^+]$ when 35.0 mL of Ag^+ has been added? (10 pts)

35.0 mL is before the equivalence point so Cl^- is still in excess. Thus we need to first determine $[\text{Cl}^-]$.

$$[\text{Cl}^-] = [n(\text{Cl}^-) - n(\text{Ag}^+)]/[V(\text{Cl}^-) + V(\text{Ag}^+)]$$

$$[\text{Cl}^-] = [(0.01188 \text{ M})(25.0 \text{ mL}) - (0.00800 \text{ M})(37.11 \text{ mL})]/60.0 \text{ mL}$$

$$[\text{Cl}^-] = [(0.2969 \text{ mmol} - (0.2800 \text{ mmol}))]/(60.0 \text{ mL}) = 2.81 \times 10^{-4} \text{ M}$$

Now, we can calculate $[\text{Ag}^+]$ in equilibrium with Cl^- : $[\text{Ag}^+] = 1.77 \times 10^{-10}/2.81 \times 10^{-4}$

$$[\text{Ag}^+] = \mathbf{6.3 \times 10^{-10} \text{ M}} \text{ (2 sig figs since the mole subtraction loses one of the three sig figs)}$$

BONUS. Calculate $[\text{Ag}^+]$ at the equivalence point. (3 pts)

At equivalence point, $[\text{Ag}^+] = [\text{Cl}^-]$. These must also be in equilibrium with solid, so the answer is the same as if we had put $\text{AgCl}(s)$ in water. $K_{\text{sp}} = 1.77 \times 10^{-10} = [\text{Ag}^+][\text{Cl}^-] = [\text{Ag}^+]^2$

Or $[\text{Ag}^+] = (1.77 \times 10^{-10})^{0.5} = \mathbf{1.33 \times 10^{-5} \text{ M}}$

4. Calculate the wavelength in nm of light with a wavenumber of 3300 cm^{-1} . (4 pts)

$$\tilde{\nu} = 3300 \text{ cm}^{-1} \text{ and } \lambda = 1/\tilde{\nu} = (1/3300 \text{ cm})(1 \text{ m}/100 \text{ cm})(10^9 \text{ nm}/\text{m}) = \mathbf{3.0 \times 10^4 \text{ nm}}$$

5. Calculate the molar concentration of benzene in a sample if the sample is placed in a cuvette with a 1.00 cm pathlength, a transmittance of 0.783 is read, and benzene has a molar absorptivity of $98.6 \text{ M}^{-1} \text{ cm}^{-1}$ at 268 nm. (8 pts)

$$T = 0.783 \text{ so } A = -\log T = -\log(0.783) = 0.106 \text{ and } A = \epsilon bC \text{ or}$$

$$C = (0.106)/(98.6 \text{ M}^{-1} \text{ cm}^{-1})(1.00 \text{ cm}) = \mathbf{1.08 \times 10^{-3} \text{ M}}$$

6. Given the following reversed-phase HPLC chromatogram and data table below, determine:

a) the retention factor for adenosine (3 pts)

$$k = (3.564 - 1.056)/1.056 = 2.375$$

(slightly different # if reading plot)

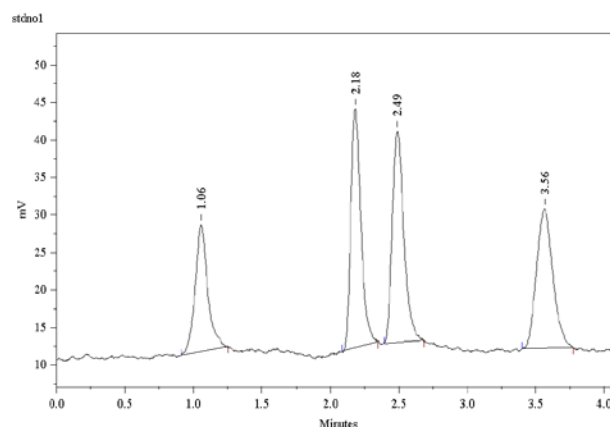
b) the resolution between
uracil and sulfanilamide (4 pts)

$$R_s = \Delta t / w_{ave}$$

$$\Delta t = 2.489 - 2.182 = 0.307$$

$$w_{ave} = 0.5(0.136 + 0.155) = 0.1455$$

$$R_s = 2.11$$



c) which compound is the least polar (explain). (3 pts)

Since reversed-phase means non-polar column, the compounds that are the most retained are the least polar – so **adenosine**

d) The plate number (N) based on the adenosine peak. (4 pts)

$$N = 16(t_r/w)^2 = 16(3.564/0.219)^2 = 16(16.3)^2 = 4240$$

e) The plate height (H) if the column used for the separation was 150 mm length x 4.6 mm diameter. (3 pts)

$$H = L/N = 150 \text{ mm}/4240 = 0.035 \text{ mm} (= 35 \mu\text{m})$$

Data Table

Peak #	Ret Time (min.)	Name	Area (mV*s)	Peak Width (min.)
1	1.056	Unretained	1074.343	
2	2.182	uracil	1617.349	0.136
3	2.489	sulfanilamide	1645.061	0.155
4	3.564	adenosine	1525.604	0.219