**Notre Dame University**
**Faculty of Natural and Applied Sciences**
**Department of Sciences**
**Quantitative Analysis / CHM 215**
**Final Exam – Duration: 120 minutes**

***Student Name:_____ID#:_____***

***Instructor: R. Dib***

**The exam is divided in 2 parts:**

**Part I:** Multiple-choice questions (11 questions, 3 points each)
**Part II:** 9 subjective questions and problems including a bonus question (72 points)

Good Luck

## Part I: Multiple-choice questions

1- The conditional formation constant (K') in EDTA titration is

a) **pH-dependent**
b) Temperature-dependent
c) EDTA concentration dependent
d) Two of the above
e) All of the above

2- Which EDTA species is the most powerful complexing form?

a) $H_4Y$
b) $H_3Y^-$
c) $H_2Y^{2-}$
d) $HY^{3-}$
e) **$Y^{4-}$**

3- Consider a solution containing a mixture of cations composed of $Hg^{2+}$, $Pb^{2+}$, and $Al^{3+}$. Given the $pK_{MY}$ (-log $K_{MY}$; M is the ion and Y the EDTA) of species below, arrange these ions according to their order of complexation when EDTA is added (i.e., which ion will be complexed first and which one will do it last).

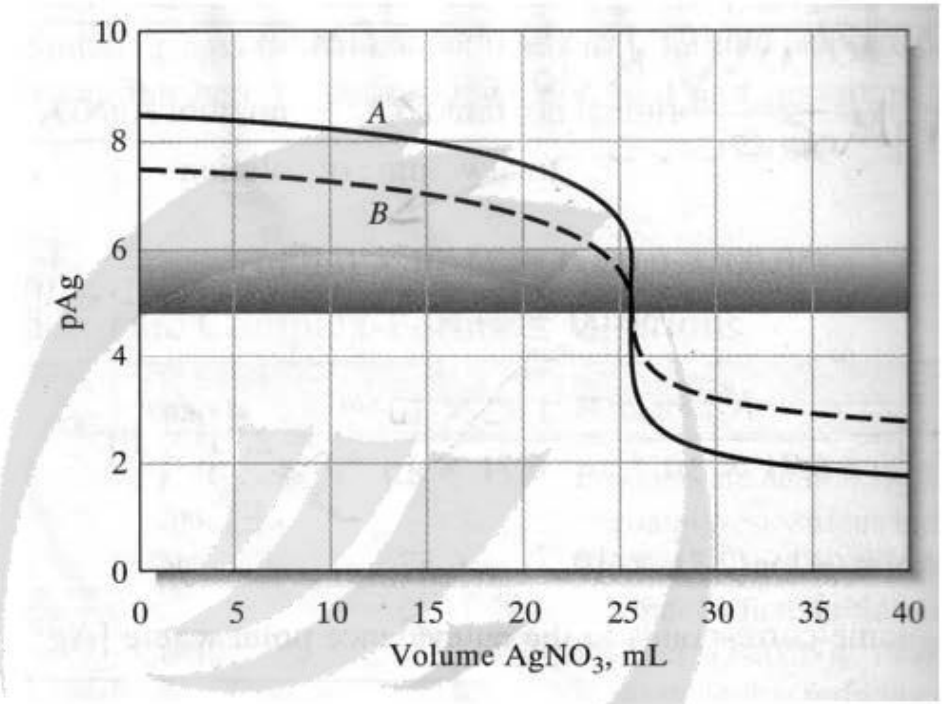
$HgY^{2-}$ = - 21.8
$PbY^{2-}$ = - 18.04
$AlY^{-}$ = -16.13

a) **$Hg^{2+}$, $Pb^{2+}$, $Al^{3+}$**
b) $Al^{3+}$, $Hg^{2+}$, $Pb^{2+}$
c) $Al^{3+}$, $Pb^{2+}$, $Hg^{2+}$
d) $Pb^{2+}$, $Hg^{2+}$, $Al^{3+}$
e) Not enough information is given to correctly answer the question

4- In the Fajans method for signaling the end point in argentometric titration:

a) The indicator used is an adsorption indicator
b) The indicator used is fluoroscein
c) The end point is indicated by back titration
**d) Two of the above**
e) All of the above

Questions 5 to 8: Answer the questions regarding the titration curves of $Cl^-$ with Ag+ shown below.




5- To which kind of titration this example belongs?

a) Complexation titration
b) Organic complex formation titration
**c) Inorganic precipitation titration**
d) Organic precipitation titration
e) Inorganic complexation titration

6- Explain the difference between curve A and curve B

a) In curve A, both the titrant and the analyte are less concentrated than in curve B
**b) In curve A, both the titrant and the analyte are more concentrated than in curve B**
c) In curve A, only the titrant is more concentrated than in curve B
d) Since the equivalence point is the same in both curves, the titrant and the analyte have the same concentration; the difference is due to different pH values

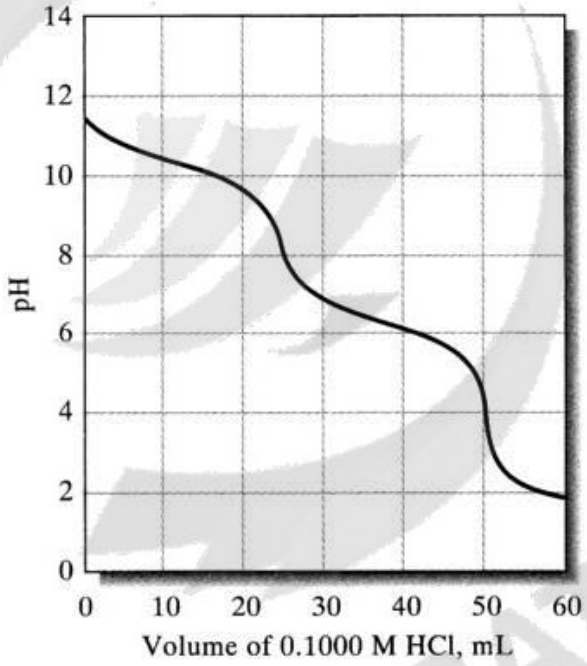
7- Is the indicator used in this titration suitable to monitor the titration of $Cl^-$ in both cases (A and B)?

**a) Yes**
b) No
c) Maybe
d) We cannot tell since we didn't practice such case in class

8- What approximate $pK_{sp}$ value for AgCl can be deduced form the graph above?

a) 2
b) 5
c) 6
d) 8
**e) 10**

Questions 9 to 11: Consider the titration curve below




9- Describe the composition of a solution that would be expected to yield a curve resembling the above curve

a) Solution containing a difunctional weak acid
b) Solution containing a difunctional strong acid
**c) Solution containing a difunctional weak base**
d) Solution containing a difunctional strong base

10- What is the approximate pH when the neutralization titration is completed?

a) 10
b) 8
c) 6
**d) 4**
e) 2

11- At which approximate pH the concentration of the amphiprotic (if any) is the largest?

a) 10
**b) 8**
c) 6
d) 4
e) None of the above

## Part II: subjective questions and problems

1- Write the overall chemical equation and equilibrium constant expression for the formation of the complex $Ag(S_2O_3)_2^{3-}$. (5 points)

2- Calculate the pCa in a solution obtained by adding 30 mL of a 0.01 M EDTA solution to 50 mL of a 0.005 M $Ca^{2+}$ solution at pH 10.0 ($K_{CaY} = 5 \times 10^{10}$). (10 points)

**Answer: $[Ca^{2+}] = 2.86 \times 10^{-10}$; pCa = 9.54**

3- Calculate the pH of a solution that is 0.040 M in

A) $Na_3PO_4$ (5 points)

**Answer: 12.47**

B) $Na_2HPO_4$ (5 points)

**Answer: 9.7**

4- A silver nitrate solution contains 14.77 g of primary-standard $AgNO_3$ in 1.00 L. What volume of this solution will be needed to react with 381.1 mg of $BaCl_2.2H_2O$? (6 points)

**Answer: 35.8**

5- A 48.0% (w/w) aqueous HBr (80.91 g/mol) solution has a density of 1.5 g/mL.

i) What is the analytical concentration of HBr? (5 points)

**Answer: 8.9 M**

ii) Why is it more accurate to state concentration as "analytical concentration" than as "equilibrium concentration" in this case? (2 points)

**Answer: they are equal**

iii) HBr is a strong acid. What is the approximate equilibrium concentration of HBr and its dissociation species? (3 points)

**Because the HBr dissociated in solution. The concentration of $Br^-$ is about 8.9 M.**

6- Solubility Equilibria: Calomel, $Hg_2Cl_2$, (MW: 472.09) dissolves to form $Hg_2^{2+}$ and chloride with a $K_{sp}=1.2\times10^{-18}$. Calculate the mass of calomel that will dissolve in:

A) 1.00 L pure water (5 points)

B) 1.00 L of a 0.030 M solution of NaCl (5 points)

**A)**

**The equilibrium equation is**

$$Hg_2Cl_2\ (s) \leftrightarrows Hg_2^{2+}\ (aq) + 2Cl^-\ (aq)$$

**Using the table method,**

| | $Hg_2Cl_2$ (s) | $Hg_2^{2+}$ (aq) | $Cl^-$ (aq) |
|---|---|---|---|
| initial | solid | 0 | 0 |
| change | $-x$ | $+x$ | $+2x$ |
| final | solid | $x$ | $2x$ |

**Solve the $K_{sp}$ equation for the molar solubility, $x$**

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)(2x)^2 = 4x^3$$

$$x = \sqrt[3]{K_{sp}/4} = \sqrt[3]{1.2\times10^{-18}/4} = 6.7\times10^{-7}\ \frac{mole}{L}$$

**Now find the weight in dissolved in 1.00 L pure water**

$$1.00L\left(\frac{6.7\times10^{-7}\ mole\,Hg_2Cl_2}{L}\right)\left(\frac{472.09g\,Hg_2Cl_2}{mole\,Hg_2Cl_2}\right) = 3.16\times10^{-4}\,g\,Hg_2$$

**B)**

**The equilibrium equations are**

$$Hg_2Cl_2\ (s) \leftrightarrows Hg_2^{2+}\ (aq) + 2Cl^-\ (aq)$$

$NaCl\ (s) \leftrightarrows Na^+\ (aq) + Cl^-\ (aq)$

**Using the table method,**

| | $Hg_2Cl_2$ (s) | $Hg_2^{2+}$ (aq) | $Cl^-$ (aq) |
|---|---|---|---|
| **initial** | **solid** | **0** | **0.030** |
| **change** | **-*x*** | **+*x*** | **+2*x*** |
| **final** | **solid** | ***x*** | **0.030 + 2*x*** |

**Since the chloride concentration produced from $Hg_2Cl_2$ dissolution in pure water is only $2x = 1.34 \times 10^{-6}$, 2x can be neglected relative to the 0.030 M chloride from NaCl. We solve the $K_{sp}$ equation for the molar solubility, *x***

$$K_{sp} = [Hg_2^{2+}][Cl^-]^2 = (x)(0.030 + 2x)^2 \approx x(0.030)^2$$

$$x = \frac{K_{sp}}{(0.030)^2} = \frac{1.2 \times 10^{-18}}{0.0009} = 1.3 \times 10^{-15}\ \frac{mole}{L}$$

**Now find the weight in the 0.030 M chloride solution**

$$1.00\,L\left(\frac{1.3 \times 10^{-15}\ mole\,Hg_2Cl_2}{L}\right)\left(\frac{472.09\,g\,Hg_2Cl_2}{mole\,Hg_2Cl_2}\right) = 6.29 \times 10^{-13}\,g\,Hg_2Cl_2$$

7- Assuming a density of 1 g/mL, determine the number of ppm of phosphorus in a $5.32 \times 10^{-6}$ M $Na_3PO_4$ solution. (6 points)

**Answer: 0.165 ppm**

8- A 25.00-mL sample containing $Fe^{3+}$ was treated with 10.00 mL of 0.0367 M EDTA to complex all the $Fe^{3+}$ and leave excess EDTA in solution. The excess EDTA was then back-titrated, requiring 2.37 mL of 0.0461 M $Mg^{2+}$.

A) What was the concentration of $Fe^{3+}$ in the original solution? (7 points)

**Answer: 0.01 M**

B) What was the percentage (mass by volume) of $Fe^{3+}$ in the original solution? (3 points)

**Answer: 0.0576**

BONUS:

1- Why the smaller the Ksp of a salt obtained in argentometric titration, the more complete the reaction between silver ions and the anions of the salt? (5 points)

**Answer: because the smaller the Ksp, the smaller the concentrations of ions at equilibrium**