1. (10) Organic precipitants have been used for the analysis of inorganic ions for many years, often because of a greater selectivity of the organic precipitating agents than of the simple inorganic ions. Two classic examples of organic precipitating agents are dimethylglyoxime and oxine or 8-hydroxyquinoline. Compare and discuss these two precipitants for the analysis of inorganic cations.

2. (10)
   a. (5) A solution with a pH of 7.4 contains some binary combination of $\text{H}_2\text{PO}_4$, $\text{NaH}_2\text{PO}_4$, $\text{Na}_2\text{HPO}_4$, or $\text{Na}_3\text{PO}_4$. A 50.00 mL aliquot of the solution is titrated to the thymolphthalein end point (pH range = 9.3 – 10.5) with 24.30 mL of 0.1005 N NaOH. Another 50.00 mL aliquot of the solution is titrated to the bromcresol green end point (pH range = 3.8 – 5.4) with 30.55 mL of 0.1208 N HCl. Calculate the molar concentrations of the two phosphate species.

   b. (5) Phosphate buffers can be prepared from the readily available alkali metal salts and standard solutions of acids or bases. What volume of 0.105 F{HCl} or what volume of 0.110 F{NaOH} must be added to a 250 mL of 0.192 F{NaH$_2$PO$_4$} to make a buffer at pH = 2.80?

3. (15)
   a. (5) EDTA titrations have been standard methods for analysis of aqueous solutions of metal ions for many years. The procedures are very specific about pH for the titrations. Explain why $\text{Al}^{3+}$, but not $\text{Mg}^{2+}$, can be determined by titration with EDTA at pH = 4.

   b. (5) Calculate $[\text{Al}^{3+}]$, mol/L, after the addition of 25.0 mL of 0.01068 F{EDTA} to 35.0 mL of 0.00763 M{Al$^{3+}$} at pH = 6.00.

   c. (5) Some metal ions, {Ag$^+$, for example} do not form strong complexes with EDTA or do not have satisfactory indicators. (Although, why anyone would analyze Ag$^+$ solutions with EDTA is another question). However, one can be devious (or clever) by using chemical reactions to produce ions that can easily be analyzed using EDTA.

   The Ag$^+$ ions in a 25.00 mL aliquot were converted to Ag(CN)$_2^-$ ions by the addition of 35.00 mL of 0.0800 F Ni(CN)$_4^{2-}$ and the liberated Ni$^{2+}$ ions were titrated with 43.70 mL of 0.02400 F{NaH$_2$EDTA}. Calculate [Ag$^+$] in the original solution.
4. (10) The plots below represent the equilibrium solubility of AgCl(s) (a) in solutions of HNO₃ (●), and (b) in solutions of NaCl (■), expressed as S/S₀, where S₀ represents the solubility of AgCl in pure water, 1.3*10⁻⁵ M. Explain each set of observations. Algebraic and/or chemical equations are required in your explanations. Don’t attach any special significance to the exact shapes of the curves; they are Excel “smooth” curves through the points. What is the analytical significance of these observations for the gravimetric determination of Ag as AgCl(s)?

![Graph of solubility vs molarity of electrolyte]

5. (10) A mixture containing only CaC₂O₄ and MgC₂O₄ was heated on a recording thermobalance. Inadvertently, the initial weight was not recorded. However, the sample was heated to a constant weight of 0.4123 g of CaCO₃ and MgO. {The decomposition products are known for CaC₂O₄ and for MgC₂O₄.} Heating to a higher temperature gave a second plateau (constant weight of sample) of 0.2943 g of CaO and MgO. Calculate weight percent CaC₂O₄ in the original sample.

6. (10) The determination of Ag has been important in analytical chemistry for much longer than a century. The reaction of Ag⁺ with chloride was used by T. W. Richards and his students (~1900) for the determination of atomic weights of metals from the metal chlorides. The common methods for the detection of the end points for the determination of Cl⁻ concentrations are (a) the Mohr method (using CrO₄²⁻ as the indicator, 1856) and (b) the Fajans (1923) method, using dichlorofluorescein as the indicator. (c) The standard volumetric method for the determination of Ag (Volhard, 1874) uses CNS⁻ as the precipitating ion and Fe³⁺ as the indicator.

Explain how (a), (b), or (c) works and explain how you would determine either Ag⁺ or Cl⁻ without using these indicators. Analyses of Ag composition in coinage were done before 1856.
7. (10) The plots below contain data for the solubility of CaSO$_4$ in pure water and in solutions of different concentrations of NaCl (●) and KNO$_3$ (■) in curve (a) and (NH$_4$)$_2$SO$_4$ (▲) and MgSO$_4$ (●) in curve (b). The solubility of CaSO$_4$ in pure water is 0.0153 M. Explain each curve. The shapes of the curves are determined by Excel fits to the data and should not be over interpreted. Algebraic and/or chemical equations are required in your answer.

![Solubility of CaSO$_4$](image)

8. (10) Weathering of statues, tombstones, and buildings and the formation of stalactites and stalagmites are obvious results of the interactions of acid/base reactions and solubilities of ionic salts. The solubilities of metal sulfides (often with ridiculously small $K_{sp}$ values) provide additional examples of this phenomenon of multiple equilibria. Calculate the solubility of CuS(s) in water maintained at pH 7.00, including hydrolysis effects.

9. (10) There is a “neat” demonstration (well, I think so) which shows the interactions of solubilities and complexation for silver salts. A precipitate of AgCl is formed from dilute Ag$^+$ and is then dissolved in moderately concentrated aqueous ammonia. Then a precipitate of AgBr is formed by addition of NaBr to the clear solution of the silver/ammine complexes. Derive an equation for the solubility of AgCl in aqueous ammonia in terms of [NH$_3$] and the formation constants, $K_{F1}$ and $K_{F2}$, for the silver/ammine complexes, Ag(NH$_3$)$_2^+$ and Ag(NH$_3$)$_3^+$. {Don’t worry about the subsequent precipitation of AgBr.}
10. (5) There are named reactions in organic chemistry and named equations in physical chemistry and named reagents and or processes in analytical chemistry. One of the most famous (infamous) is the Karl Fisher reagent. What is the reagent used for, what is it, and how does it work?

Possibly useful information:
\[ E^0 \{ \text{Ce}^{4+} \rightarrow \text{Ce}^{3+} \} = +1.44 \text{ V} \quad E^0 \{ \text{TI}^{3+} \rightarrow \text{TI}^+ \} = 1.28 \text{ V} \]

\[ \begin{align*}
\text{H}_3\text{PO}_4: \quad K_{A1} &= 7.1 \times 10^{-3} \\
K_{A2} &= 6.3 \times 10^{-8} \\
K_{A3} &= 4.2 \times 10^{-13} \\
K_{F}\{\text{MgEDTA}^2-\} &= 4.9 \times 10^8 \\
K_{F}\{\text{AlEDTA}^-\} &= 1.3 \times 10^{16} \\
K_{S}\{\text{CuS}\} &= 8.0 \times 10^{-37} \\
K_{A1}\{\text{H}_2\text{S}\} &= 9.5 \times 10^{-8} \\
K_{A2}\{\text{H}_2\text{S}\} &= 1.3 \times 10^{-14}
\end{align*} \]

pH \quad \alpha_4\{\text{EDTA}\}
\begin{align*}
3.00 & \quad 2.5 \times 10^{-11} \\
4.00 & \quad 3.6 \times 10^{-9} \\
6.00 & \quad 2.2 \times 10^{-5} \\
8.00 & \quad 5.4 \times 10^{-3} \\
10.00 & \quad 0.35 \\
11.00 & \quad 0.85
\end{align*}