Q1.

a) Using the proper number of significant figures what is the formula weight of \( \text{K}_2\text{Cr}_2\text{O}_7 \) and the uncertainly? Use atomic weights as: \( \text{K} \) 39.0983 ± 0.0003, \( \text{Cr} \) 51.9961 ± 0.0006, and \( \text{O} \) 15.9994 ± 0.0003 (7 pts)

Formular weight of \( \text{K}_2\text{Cr}_2\text{O}_7 \) = \( 2(39.0983) + 2(51.9961) + 7(15.9994) \)
= 294.1846 (7 S.F.) (1 pt/each factor)

Uncertainly = \( [2(0.0003)^2 + 2(0.0006)^2 + 7(0.0003)^2]^{1/2} \) = 0.0012369 (3 pts for uncertainly)

Formular weight of \( \text{K}_2\text{Cr}_2\text{O}_7 \) = 294.1846 ± 0.0012

Wrong significant figure (S.F.) 1 pt/ each answer of formular weight and uncertainly

b) How many grams of \( \text{K}_2\text{Cr}_2\text{O}_7 \) are required to prepare 250.00 ml of 0.0500 M \( \text{Cr}_2\text{O}_7^{2-} \)? (8 pts)

\[
0.25000 \text{ L} \times 0.0500 \text{ mol/L} \times 1 \text{ mol K}_2\text{Cr}_2\text{O}_7 \times 294.1846 \text{ g/mol} = 3.6773075 = 3.68 \text{ g}
\]

1 pt/each factor and 4 pts/final answer
Wrong significant figure (S.F.) 1 pt

c) Sometimes we will dry chemicals such as KHP, EDTA before we use them, Is this process (drying) necessary to do? Why or why not? (5pts)

Yes, if those chemicals are the primary standard and hydroscopic compound then you need to dry them first before you use them. Because their masses will be interfered by air moisture (water), your results will not be nearly 100% accurate.

No, if you correct mass of those chemicals with buoyancy equation and use true mass for calculation such as you did with Tris in exp.5

If your answer is either of these answers, you get 5 pts
If your answer mentions to other purities or other substances, you have indicate them: “What are they?” , Why? And How? Up to 4pts take off, it depends your answer
Totally wrong (No pts)
Q2.

2. A certain procedure required the preparation of ~0.1 M HCl and ~0.01 M NaOH. The molarities of these solutions were determined by standardization with Na₂CO₃ and KHP, respectively. Four titrations of Na₂CO₃ with ~0.1 M HCl and KHP with ~0.01 M NaOH were performed, and the calculated molarities for the HCl and NaOH solutions were as follows: 0.1012, 0.1009, 0.1015, and 0.1008 mol/L for HCl solution; 0.01151, 0.01097, 0.01099, 0.01096 mol/L for the NaOH solution.

a. Perform the Q test to determine if it is necessary to discard any of the calculated molarities for HCl or NaOH. (6 points)

For HCl:

- \( Q_{calc} = \frac{\text{gap}}{\text{range}} = \frac{0.1015 - 0.1012}{0.1015 - 0.1008} \)
  \[ = 0.43 \rightarrow \text{keep (<Q_{table}(0.76))} \]

- \( Q_{calc} = \frac{0.1009 - 0.1008}{0.1015 - 0.1008} \)
  \[ = 0.14 \rightarrow \text{keep (<Q_{table}(0.76))} \]

+2 for performing Q test for HCl (+3 if only Q test for HCl)

For NaOH:

- \( Q_{calc} = \frac{0.01151 - 0.01099}{0.01151 - 0.01096} \)
  \[ = 0.95 \rightarrow \text{discard (>Q_{table}(0.76))} \]

- \( Q_{calc} = \frac{0.01097 - 0.01096}{0.01151 - 0.01096} \)
  \[ = 0.02 \rightarrow \text{keep (<Q_{table}(0.76))} \]

+2 for performing Q test for NaOH (+3 if only Q test for NaOH)

Discard 0.01151 M

Q (90% confidence) Number of Observations
0.76 4
0.64 5
0.56 6

b. Calculate the mean molarities and standard deviations of the HCl and NaOH solutions. (8 points)

- \( \bar{x}_{\text{avg}}(\text{HCl}) = \frac{\sum x_i}{N} = \frac{0.1012 + 0.1009 + 0.1015 + 0.1008}{4} = 0.1011 \text{ M} \)
  +2 for correct answer and setup
  *Answer same if Q test was or was not performed on HCl.

- \( s(\text{HCl}) = \sqrt{\frac{\sum (x_{avg} - x_i)^2}{(N-1)}} = \sqrt{\frac{0.0003}{4-1}} = 0.0003 \)
  +2 for correct answer and setup
  *Answer same if Q test was or was not performed on HCl.

- \( \bar{x}_{\text{avg}}(\text{NaOH}) = \frac{0.01097 + 0.01099 + 0.01096}{3} = 0.01097 \text{ M} \)
  +2 for correct answer and setup

*\( \bar{x}_{\text{avg}} = 0.01111 \text{ M} \) if Q test was not performed on NaOH.
c. Using the mean molarities of the HCl and NaOH solutions, calculate the $H^+$ concentration and the $pH$ in each solution. $K_w = 1.01 \times 10^{-14}$ (6 points)

- **0.1011M HCl $\rightarrow H^+ + Cl^-$**
  - $[H^+] = 0.1011M$ since HCl completely dissociates
  - $pH = -\log(0.1011) = 0.9952$

- **0.01097M NaOH $\rightarrow Na^+ + OH^-$**
  - $[OH^-] = 0.01097M$ since NaOH completely dissociates
  - $[H^+] = 1.01 \times 10^{-14} / 0.01097M = 9.21 \times 10^{-13}$
  - $pH = -\log(9.21 \times 10^{-13}) = 12.036$

  * $[H^+] = 9.09 \times 10^{-13}M$ if 0.01111M was used for $[NaOH]$. ($\pm 1$ for correct answer and setup)
  * $pH = 12.041$ if $9.09 \times 10^{-13}$ was used for $[H^+]$.

**Only 1 point off for SF for entire question**
Q3

1) The formation constant ($K_f$) of CaY$_2^-$ is $4.9 \times 10^{10}$. Calculate the concentration of free Ca$^{2+}$ in a solution of 0.15 M CaY$_2^-$ at pH 10. At pH 10, $\alpha_{Y^{4-}}$ is 0.36. You may use that [Ca$^{2+}$] is much smaller than 0.15 M and so 0.15 M - x ~ 0.15 M, where [Ca$^{2+}$] = x.

$$K_{f}' = K_f \cdot \alpha_{Y^{4-}}$$  \hspace{1cm}  (2pts)  \hspace{1cm}  K_{f}' = \frac{[CaY^{-2}]}{([Ca^{2+}][EDTA])} \hspace{1cm} (2pts)$$

$$K_f \cdot \alpha_{Y^{4-}} = \frac{[CaY^{-2}]}{([Ca^{2+}][EDTA])} \hspace{1cm} (2pts)$$

$$4.9 \times 10^{10} \cdot 0.36 = \frac{[0.15 - x]}{[x \cdot x]} \hspace{1cm} (2pts)$$

$$0.15 - x = 0.15 \hspace{1cm} (2pts)$$

$$1.764 \times 10^{10} = 0.15/x^2 \hspace{1cm} (No \ more \ than \ 6pts \ for \ eqs.; \ 3 \times 2 \ pts)$$

$$x = 2.9 \times 10^{-6} \ M \hspace{1cm} (2pts)$$

SF for square roots was not covered. So no points off for SF on this answer.

2) A solution containing 25.00mL of ~5 M HCl is titrated by adding 50.00mL of 3.267M NaOH, and then the excess NaOH is titrated with 23.24mL of a KHP solution (MW=204.221). The KHP solution was prepared by dissolving 0.8567g of KHP in 40.00mL of H$_2$O.

a) Calculate the Molarity of the KHP solution. 1pt for Eq. 3pts for Answer

$$\frac{0.8567 \text{g KHP}}{204.221 \text{ (g/mole)} \cdot (1/0.04000 \text{L})} = 0.1049 \text{ M}$$

b) Calculate the number of moles of NaOH added. 1pt for Eq. 3pts for Answer

$$\frac{.050000 \text{L} \cdot 3.267 \text{M NaOH}}{\text{= 0.1634 moles NaOH}}$$

b) Calculate the number of moles of NaOH added. 1pt for Eq. 3pts for Answer

$$0.1634 \text{ moles NaOH - 0.02438 moles NaOH = 0.1390 moles HCl}$$

$$0.1390 \text{ moles HCl / 0.02500 L = 5.561 M} \hspace{1cm} (2pts)$$
A compound has a molecular mass of 450.83 was dissolved in a 5-ml volumetric flask. A 1.00 ml aliquot was withdrawn, placed in a 50.0-ml volumetric flask, and diluted to the mark. The absorbance at 340 nm was 0.427 in a 1.00 cm cuvet. The molar absorptivity for this compound at 340 nm is 6454 M⁻¹cm⁻¹. A blank solution was also measured at 340 nm and the absorbance of the blank was found to be 0.013.

a) Calculate the concentration of the compound in the cuvet.

\[ A = (0.427 - 0.013) = 0.414 \]  
\[ A = \varepsilon bC \]  
\[ C = \frac{0.414}{(6454 \text{ M}^{-1}\text{cm}^{-1})(1.00\text{ cm})} = 6.41 \times 10^{-5} \text{M} \]  
(1 point for math, 1 point for answer, 1 point for unit)

b) How many milligram of compound were used to make the 5-ml solution?

Sample had been diluted *50.0ml/1.0ml
\[ C = \frac{50}{1}(6.41 \times 10^{-5} \text{M}) = 0.0032 \text{M} \]  
(3 points for dilution, 1 point for answer)
\[ X \frac{g}{(450.83 \text{gmol}^{-1})(5.0 \times 10^{-3} \text{L})} = 0.0032 \text{ mol L}^{-1} \]  
\[ X = 0.0072 \text{g} = 7.22 \text{mg} \]  
(4 points for calculations, 1 point for answer, 1 point for units)

c) If one prepare a 0.005 M standard solution of the same compound. What is the absorbance of the standard solution measured at 340 nm?

\[ A = \varepsilon bC \]  
\[ A - 0.013 = (6454 \text{ M}^{-1}\text{cm}^{-1})(1.00\text{cm})(0.005\text{M}) \]  
\[ A = 32.3 \]  
(1 point)
Q5. 1) (a) 8 points (b) 4 points 2) 8 points

1) Consider the titration of 100.0 mL of 0.0100 M Ce$^{4+}$ in 1 M HClO$_4$ by 0.0500 M Fe$^{2+}$ to give Ce$^{3+}$ and Fe$^{3+}$, using Pt and calomel reference Hg|Hg$_2$Cl$_2$ electrodes to find the end point.

\[ E = 0.767 - 0.05916 \log([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) - 0.241 \ (V) \]
\[ E = 1.70 - 0.05916 \log([\text{Ce}^{3+}]/[\text{Ce}^{4+}]) - 0.241 \ (V) \]

a) Calculate E at the following volume ($V_{Fe}$) of Fe$^{2+}$, $V_{Fe} =$ 2 mL and 30.0 mL.

b) Calculate the concentration of Ce$^{3+}$ when $V_{Fe} = 10.0$ mL.

For a mistake in the significant figure, 1 point is subtracted.

1. a)
First, obtain $V_{Fe}$ at the equivalence point ($V_e$).

\[ V_e = \frac{C_{Ce^{4+}}V_{Ce^{4+}}}{C_{Fe^{2+}}} = 100.0 \text{ mL} \times 0.0100 \text{ M} / 0.0500 \text{ M} = 20.0 \text{ mL} \ (2 \text{ points}) \]

When $V = 2$ mL, Use $[\text{Ce}^{3+}]/[\text{Ce}^{4+}]$ and obtain the ratio.

\[ E = 1.70 - 0.05916 \log([\text{Ce}^{3+}]/[\text{Ce}^{4+}]) - 0.241 \\
= 1.70 - 0.05916 \log((V/(V-V_e)) - 0.241 \\
= 1.70 - 0.05916 \log((2/18)) - 0.241 \\
\text{(2 point)} \ (\text{If } [\text{Ce}^{3+}] \text{ and } [\text{Ce}^{4+}] \text{ are calculated without } V_e \ (3 \text{ points})) \\
\text{Note: No points if the equation for Fe is used or the concentration ratio is incorrect.} \]

\[ E = 1.51 \text{ V} \ (\text{Correct calculation 1 point}) \]

When $V = 30$ mL, Use $[\text{Fe}^{2+}]/[\text{Fe}^{3+}]$ and obtain the ratio

\[ E = 0.767 - 0.05916 \log([\text{Fe}^{2+}]/[\text{Fe}^{3+}]) - 0.241 \\
= 0.767 - 0.05916 \log((V-V_e)/V_e) - 0.241 \\
= 0.767 - 0.05916 \log((10.0 \text{ mL})/(20.0 \text{ mL})) - 0.241 \ (2 \text{ points}; \text{No points if the equation for Ce is used}) \\
= 0.5438 \text{ V} \ (1 \text{ point}) \]
1. b) Calculate the concentration of Ce³⁺ when V = 10.0 mL.

\[ [\text{Ce}^{3+}] = [\text{Ce}^{4+}] \quad (V - V_e = V) \]

\[ [\text{Ce}^{3+}] = \frac{(0.0100 \text{ M} \times 100.0 \text{ mL} - 0.0500 \text{ M} \times 10.0 \text{ mL})}{(100.0 + 10.0) \text{ mL}} \quad (3 \text{ points}) \]

\[ = \frac{0.000500 \text{ moles}}{0.11 \text{ L}} = 4.54 \text{ mM} \quad \text{(Calculation 1 point)} \]

Q5. 2) Find the pH and concentration of (CH₃)N and (CH₃)NH⁺ in a 0.080 M solution of trimethylaminium chloride ((CH₃)NH⁺Cl⁻). The pKa of (CH₃)NH⁺ is 9.8000. You can neglect the effect of Cl⁻.

\[ \text{Ka} = 10^{-pK_a} = 10^{-9.8000} = 1.584 \times 10^{-10} \quad (2 \text{ points; No points if the definition of pKa is incorrect}) \]

\[ \text{(CH₃)NH⁺} \Leftrightarrow \text{Ka} \rightarrow \text{(CH₃)N} + \text{H}^+ \]

\[ \text{F} - x \quad x \quad x \quad \text{F} = 0.0800 \text{ M} \]

\[ \text{Ka} = \frac{x^2}{(\text{F}-x)} \sim \frac{x^2}{\text{F}} \quad \text{(assume F >> x)} \rightarrow \]

\[ x = (\text{KaF})^{1/2} = (1.584 \times 10^{-10} \times 0.080)^{1/2} \]

\[ x = 3.56 \times 10^{-6} \text{ M} \ll \text{F} \quad (1 \text{ point}) \]

Or you can use \[ x^2 + \text{Ka}x - \text{KaF} = 0 \].

\[ x = \left\{ -\text{Ka} \pm (\text{Ka}^2 + 4\text{KaF})^{1/2} \right\}/2 = 3.56 \times 10^{-6} \quad (3 \text{ points}) \]

\[ \text{pH} = -\log(x) = -\log(3.56 \times 10^{-6}) \quad (1 \text{ point}) \]

(no points if x is not properly obtained)

\[ \text{pH} = 5.448 \quad (1 \text{ point}) \]

Alternative answer

\[ \text{pH} = \text{pKa} + \log[(\text{CH₃}N)/\text{[(CH₃)NH⁺]}] \quad (2 \text{ points}) \quad (10-16) \]

\[ = \text{pKa} + \log[(\text{CH₃}N)] - \log[\text{CH₃NH⁺}] \]

\[ \text{pH} = \text{pKa} - \text{pH} - \log(F-x) \quad (\text{pH} = -\log[x]) \]

\[ \text{pH} = \{\text{pKa} - \log(F-x)\}/2 \quad (4 \text{ points}) \]

\[ \sim (\text{pKa} - \log F)/2 = \{9.800 - \log(0.080)\}/2 = 5.448 \]

\[ X = 10^{-\text{pH}} = 3.56 \times 10^{-6} \quad (2 \text{ point}) \]

If you just answer \[(\text{CH₃}N \text{ ]} = \text{F} \] without answering as indicated above (2 points).
Q6. Extra question  Total 5 points

0.2661 g sample contained only NaCl and KBr. It was dissolved in water and required 2.00 L of 0.00150 M AgNO₃ to precipitate all Cl⁻ and Br⁻. The molecular weights of NaCl and KBr are 58.4 and 119.0, respectively. Calculate how many moles of KBr are contained in the solid sample.

The question is from Home work 7-14.

Assume the contained KBr is x mmol.

\[
\begin{align*}
\text{Ag}^- + \text{Cl}^- & \rightarrow \text{AgCl} \\
\text{Ag}^- + \text{Br}^- & \rightarrow \text{AgBr}
\end{align*}
\]

Total Ag moles is 2.00 L \times 0.00150 M = 3.00 mmol (2 points)

Total weight of NaCl and KBr is

\[
119.0 \times x \ mg + 58.4 (3.00 - x) mg = 266.1 \ mg \quad (2 \ points)
\]

\[
(119.0 - 58.4)x = 266.1 - 58.4 \times 3.00
\]

\[
x = \frac{90.9}{(119.0 - 58.4)} = 1.50 \ mmol \quad (1 \ point)
\]

♦ No points will be given to 3.00 mmol/2 = 1.5 mmol. The assumption that the AgCl and AgBr are equal in the number of moles is incorrect.