

Part I (48 points). Show your work on problems. Evaluation based on correctness, completeness and clarity. Use appropriate number of significant figures in your final result.

Data

Couple	E°, volts	Couple	E°, volts
Ce(IV), Ce ³⁺	1.44	Sn ⁴⁺ , Sn ²⁺	0.154
Tl ³⁺ , Tl ⁺	1.25	Zn ²⁺ , Zn	-0.762
Ag ⁺ , Ag	0.800	SCE	0.244 (E vs SHE)
Fe ³⁺ , Fe ²⁺	0.771	Ag, AgCl	0.222
Cu ²⁺ , Cu	0.345	Pb ²⁺ , Pb	-0.126
VO ²⁺ , V ³⁺	0.359		

1. (12) A 1.00-mL serum sample was digested with nitric acid to eliminate organic matter, and the sample was diluted to exactly 10 mL.

- a) A 2.00 mL aliquot ^(of the diluted sample) required 4.50 mL of 0.00200 M EDTA for titration at pH 10 using Calmagite indicator. Calculate the total molar concentration of Ca + Mg in the serum sample.

In 2-mL aliquot

$$C_{Ca+Mg} = \frac{n_{y \cdot mL_y}}{mL_{Ca+Mg}} = \frac{(0.00200 \text{ mmol/mL})(4.50 \text{ mL})}{2.00 \text{ mL}}$$

$$= 4.50 \times 10^{-3} \text{ M.}$$

In orig. sample

$$C_{Ca+Mg} = 4.50 \times 10^{-3} \text{ M} \left(\frac{10}{1} \right) = 0.0450 \text{ M.}$$

- b) A second 2.00-mL aliquot of the same ^(diluted sample) sample required 2.60 mL of the EDTA using Calcein indicator after the pH was adjusted to pH 12 with NaOH. At this high pH the magnesium precipitates as Mg(OH)₂ and does not react with EDTA. Calculate the individual molar concentrations of Ca and Mg in the serum sample

In 2-mL aliquot,

$$C_{Ca} = \frac{n_{y \cdot mL_y}}{mL_{Ca}} = \frac{(0.00200 \text{ mmol/mL})(2.60 \text{ mL})}{2.00 \text{ mL}}$$

$$= 2.60 \times 10^{-3} \text{ M}$$

In orig sample

$$C_{Ca} = 2.60 \times 10^{-3} \text{ M} \left(\frac{10}{1} \right) = 0.0260 \text{ M}$$

$$C_{Mg} = C_{Ca+Mg} - C_{Ca} = 0.0450 - 0.0260 = 0.0190 \text{ M.}$$

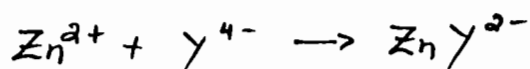
2. (12) Let us represent EDTA as H_4Y , and Y as the Y^{4-} anion. For EDTA at pH 6.00, $\alpha_Y = 2.3 \times 10^{-5}$.

a) For a 0.0100 M solution of EDTA at pH 6.00, calculate $[Y^{4-}]$.

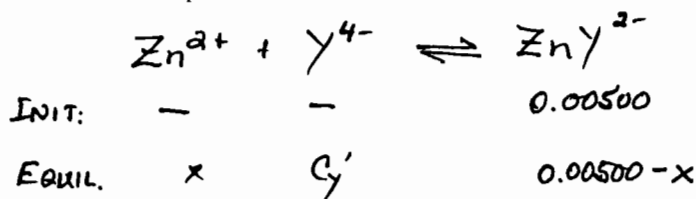
$$[Y^{4-}] = \alpha_Y C_Y = (2.3 \times 10^{-5})(0.0100 \text{ M}) = 2.3 \times 10^{-7} \text{ M}$$

b) Consider a solution prepared by addition of 50.0 mL of 0.0100 M EDTA to 50.0 mL of 0.0100 M zinc(II) sulfate at pH 6.00. For ZnY^{2-} , $K_f = 3.2 \times 10^{16}$.

i) Write a balanced chemical equation for the reaction that occurs.



ii) Calculate the equilibrium concentrations of ZnY^{2-} and Zn^{2+} in the resulting solution.



$$[Zn^{2+}] = C_Y' = x$$

$$K_f' = \frac{[ZnY^{2-}]}{[Zn^{2+}] C_Y'} = \alpha_Y K_f = (2.3 \times 10^{-5})(3.2 \times 10^{16}) = 7.4 \times 10^{11}$$

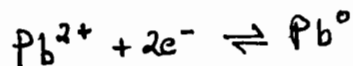
$$\approx \frac{0.00500}{[Zn^{2+}]^2}$$

$$[Zn^{2+}] \approx \sqrt{\frac{0.00500}{K_f'}} = \sqrt{\frac{0.00500}{7.4 \times 10^{11}}} = 8.2 \times 10^{-8} \text{ M}$$

$$[ZnY^{2-}] = 0.00500 - [Zn^{2+}] \approx 0.00500 \text{ M}$$

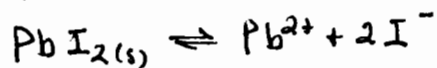
For the following questions, please refer to the table of electrode potentials on the first page.

3. (12) Calculate the potential at a lead electrode immersed in a saturated solution of lead(II) iodide containing 0.00100 M of KI. For PbI_2 , $K_{sp} = 7.9 \times 10^{-9}$.



$$E = E^{\circ}_{Pb^{2+}, Pb} - \frac{0.0592}{2} \log \frac{1}{[Pb^{2+}]}$$

Also



$$K_{sp} = [Pb^{2+}][I^-]^2$$

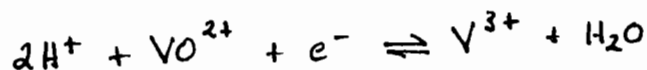
$$[Pb^{2+}] = \frac{K_{sp}}{[I^-]^2}$$

Then,

$$E = E^{\circ}_{Pb^{2+}, Pb} - \frac{0.0592}{2} \log \frac{[I^-]^2}{K_{sp}} = -0.126 - \frac{0.0592}{2} \log \frac{(1.00 \times 10^{-3})^2}{7.9 \times 10^{-9}} = -0.188 \text{ V.}$$

4. (12) Consider the following electrochemical cell.
SCE || VO^{2+} (0.100 M), V^{3+} (0.0100 M), $HClO_4$ (0.100 M) | Pt

- a) Write the half reaction and the Nernst equation for the electrode on the right, and calculate the potential at the platinum electrode.



$$E = E^{\circ}_{VO^{2+}, V^{3+}} - \frac{0.0592}{1} \log \frac{[V^{3+}]}{[VO^{2+}][H^+]^2}$$

$$= 0.359 - 0.0592 \log \frac{0.0100}{(0.100)(0.100)^2}$$

$$E_{Pt} = 0.359 - 0.0592 = 0.300 \text{ V.}$$

- b) Calculate the overall cell potential.

$$E_{cell} = E_{Pt} - E_{SCE} = 0.300 - 0.244 = 0.056 \text{ V.}$$