

(9) The reaction of EDTA with a trivalent metal ion at a pH of 4.0 may be written as:

- (a)  $M^{3+} + Y^{4-} \rightleftharpoons MY^-$   
 (b)  $M^{3+} + H_2Y^{2-} \rightleftharpoons MY^- + 2 H^+$   
 (c)  $M^{3+} + H_6Y^{2+} \rightleftharpoons MY^- + 6 H^+$

(10) When is a direct EDTA titration not useful?

- (a) When the metal precipitates in the absence of EDTA.  
 (b) When the metal reacts too quickly with EDTA.  
 (c) When the metal does not block the indicator.

(11)  $KMnO_4$  is used as the titrant in a potentiometric titration of tin(II) to tin(IV), using a S.C.E. reference electrode. After the equivalence point, you would calculate the cell voltage using the potentials of

- (a) the  $MnO_4^-/Mn^{2+}$  couple and the S.C.E.  
 (b) the  $Sn^{4+}/Sn^{2+}$  couple and the S.C.E.  
 (c) the  $MnO_4^-/Mn^{2+}$  couple and the  $Sn^{4+}/Sn^{2+}$  couple.

2. [Total 12 pts]

2.1. [6 pts] What is pH of a  $2.50 \times 10^{-7}$  M solution of HCl?

$$[H^+] = [Cl^-] + [OH^-]$$

$$[H^+] = 2.50 \times 10^{-7} + \frac{K_w}{[H^+]}$$

$$[H^+]^2 - 2.50 \times 10^{-7} [H^+] - K_w = 0$$

$$[H^+] = 2.85 \times 10^{-7} M$$

$$pH = 6.55$$

+3

2.2. [6 pts] What is the  $K_b$  of 0.050 M monoprotic base (B) if measured pH is 8.00?



$$K_b = \frac{[BH^+][OH^-]}{[B]} = \frac{x^2}{0.050 - x}$$

$$K_b = \frac{(10^{-6.00})^2}{0.050 - 10^{-6.00}} = 2.00 \times 10^{-11}$$

∵ pH = 8.00 ∴  $x = 10^{-6.00}$

3. [10 pts] Calculate to give a pH of 5.00 in the 1.00 L final diluted solution, how many grams of dipotassium oxalate (FM 166.22) should be added to 20.0 mL of 0.800 M  $HClO_4$  ( $pK_{a1}=1.27$ ,  $pK_{a2}=4.266$ )?



Initial.       $x$                        $20 \text{ mL} \times 0.8 \text{ M}$

Final         $x - 20 \times 0.8$                        $20 \times 0.8$

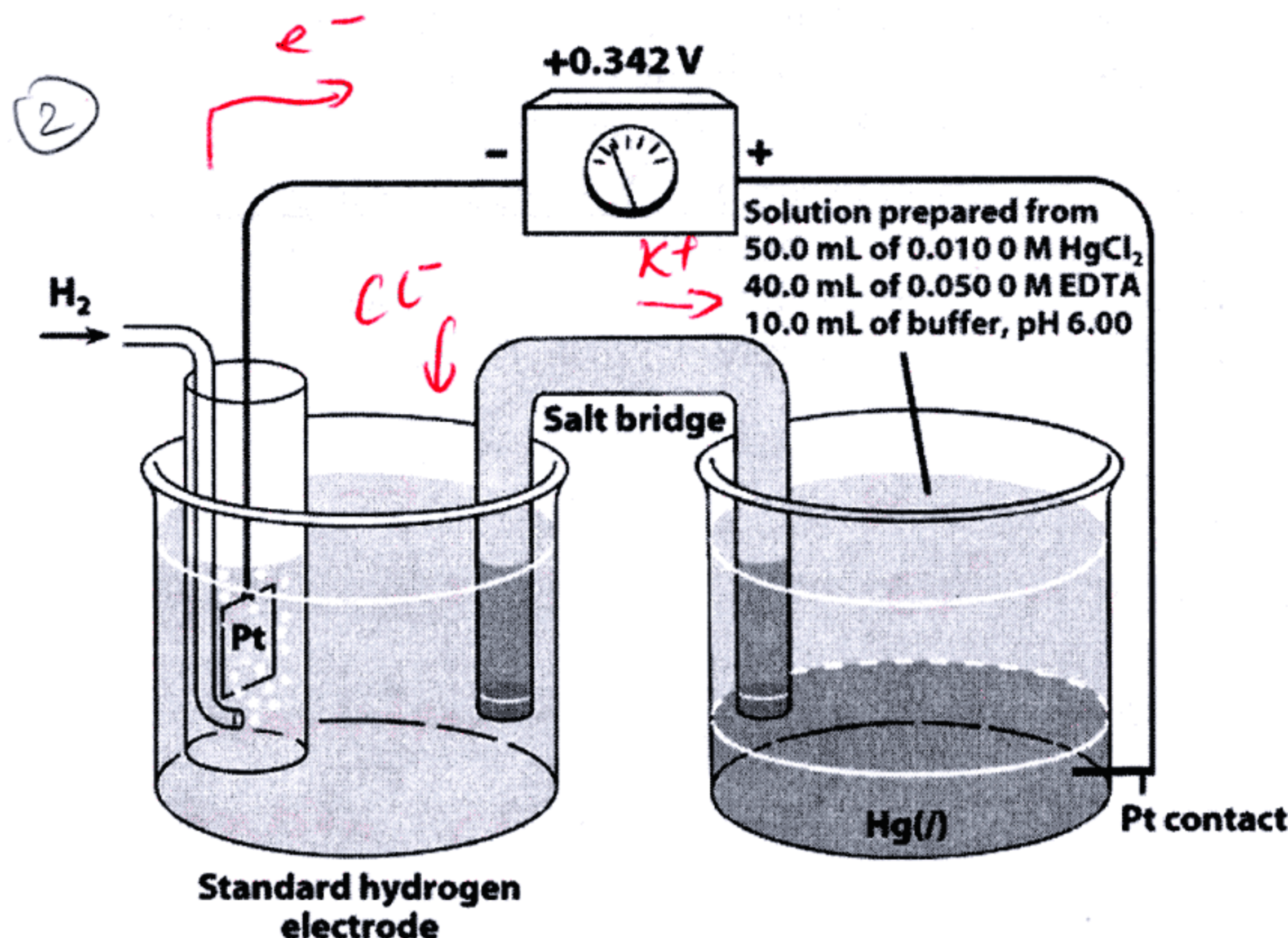
$$pH = pK_{a2} + \log \frac{[C_2O_4^{2-}]}{[HC_2O_4^-]} = 4.266 + \log \frac{x - 20 \times 0.8}{20 \times 0.8} = 5.00$$

$$x = 102.72 \text{ mmol}$$

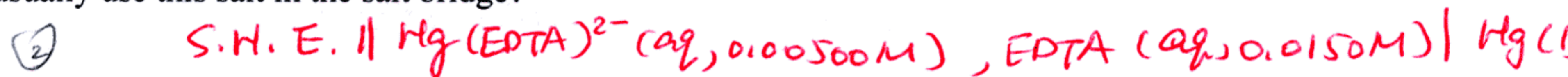
$$K_2C_2O_4 = 17.1 \text{ g}$$

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4. [Total 20 pts]



4.1. [8 pts] Write the line notation of the above cell. Draw the flow directions of electrons, cations, and anions in the graph. Give the name of the most commonly used salt in the salt bridge. Why we usually use this salt in the salt bridge?

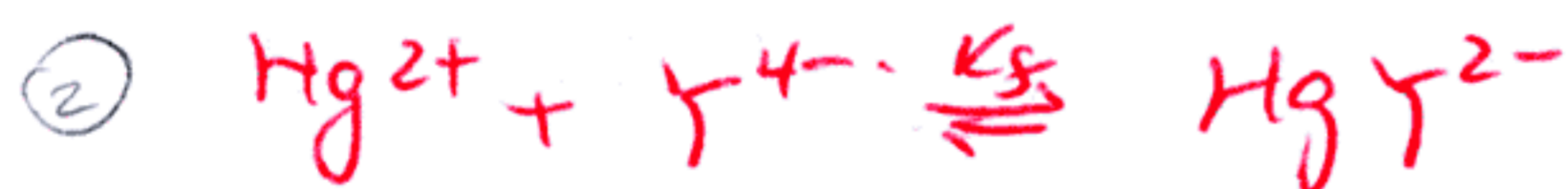


② K<sup>+</sup> and Cl<sup>-</sup> have similar mobilities. → minimize the Junction potentials at the interfaces of the salt bridge.

4.2. [12 pts] Using the information shown in the graph and E<sup>0</sup><sub>Hg<sup>2+</sup>/Hg</sub> = 0.852 V, calculate the value of K<sub>f</sub> for Hg(EDTA)<sup>2-</sup>.



② E<sub>+</sub> = 0.852 -  $\frac{0.05916}{2} \log \frac{1}{[Hg^{2+}]}$



② K<sub>f</sub> =  $\frac{[HgY^{2-}]}{[Hg^{2+}][Y^{4-}]} = \frac{[HgY^{2-}]}{[Hg^{2+}] \alpha_{Y^{4-}} [EDTA]}$

[EDTA]<sub>ex</sub> =  $\frac{40 \times 0.0500 - 50 \times 0.0100}{50.0 + 40.0 + 10.0} = 0.015 \text{ M}$

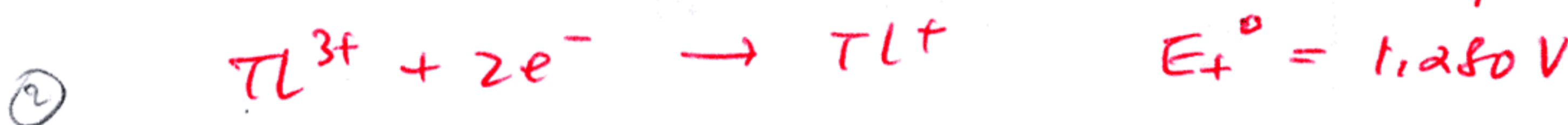
② E = 0.342 = E<sub>+</sub> - E<sub>-</sub> =  $[0.852 - \frac{0.05916}{2} \log(\frac{1}{[Hg^{2+}]})] - 0$

[Hg<sup>2+</sup>] = 5.7 × 10<sup>-18</sup>

② K<sub>f</sub> =  $\frac{0.00500}{(5.7 \times 10^{-18}) \times (1.8 \times 10^{-5}) \times (0.0150)} = 3 \times 10^{21}$

5. [8 pts] A student will perform the titration of iron(II) with thallium(III) using a S.C.E. reference electrode. Select the best indicator in the list below and give your calculation and explanation. The  $E^\circ$  for  $\text{Fe}^{3+}/\text{Fe}^{2+}$  is 0.771 V, the  $E^\circ$  for  $\text{Tl}^{3+}/\text{Tl}^+$  is 1.280, and the  $E$  for S.C.E. is 0.241 V)

| Indicator                   | Color Reduced | Color Oxidized | $E^\circ$ |
|-----------------------------|---------------|----------------|-----------|
| Methylene blue              | colorless     | blue           | 0.53      |
| Diphenylamine sulfonic acid | colorless     | red-violet     | 0.87      |
| Diphenylamine               | colorless     | violet         | 0.75      |



The indicator transition range should overlap the steepest part of the titration curve.

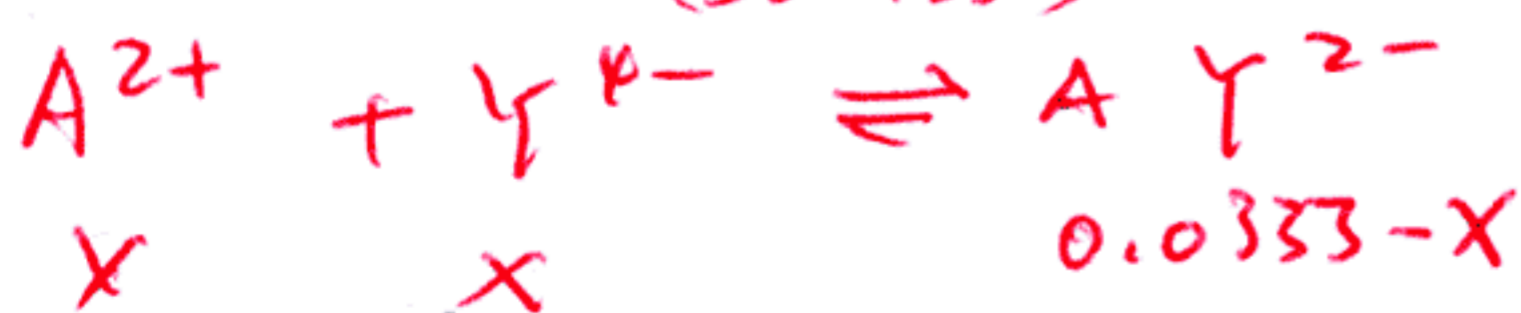
④ At EP,  $E = \frac{2 \times 1.280 + 1 \times 0.77}{2+1} - 0.241 = 0.869$

∴ Diphenylamine sulfonic acid.

6. [12 pts] 50 mL of 0.0500 M metal ion  $\text{A}^{2+}$  is titrated with 0.1000 M EDTA at pH 10.00. The  $K_f$  of  $\text{A}^{2+}$  is  $1.3 \times 10^{10}$ . 50 mL of 0.0500 M the other divalent metal ion,  $\text{B}^{2+}$ , is also titrated with 0.1000 M EDTA at pH 10.00. The  $K_f$  of  $\text{B}^{2+}$  is  $1.6 \times 10^8$ . Calculate the volume of EDTA needed at the equivalence point. Draw the theoretical titration curves for the two reactions and indicate the equivalence points of the two reactions in the curves. (Note: you don't need to do further calculation, but give the relative positions of the curves and the equivalence points in the graph).

③ At EP, need  $\frac{50 \times 0.0500}{0.100} = 25\text{ mL EDTA}$

$[\text{AY}^{2-}] = \frac{0.0500 \times 50\text{ mL}}{(50+25)\text{ mL}} = 0.0333\text{ M}$



③  $\frac{0.0333 - x}{x^2} = K_f' = \alpha_{Y^{4-}} \cdot K_f = 0.30 \times 1.3 \times 10^{10} = 3.9 \times 10^9$

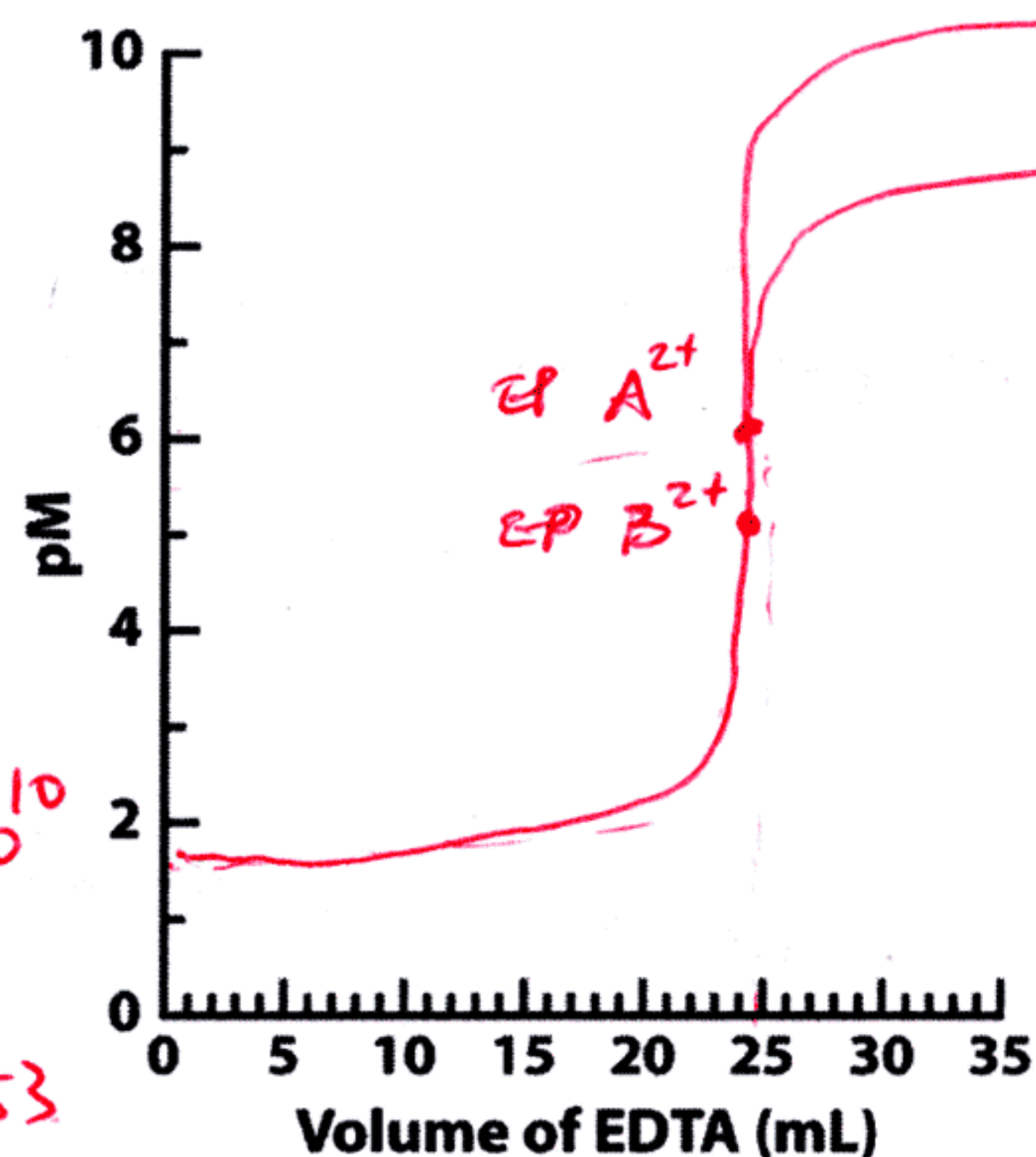
$x_{\text{A}^{2+}} = 2.92 \times 10^{-6}\text{ M}$

$\text{pA}^{2+} = 5.53$

For  $\text{B}^{2+}$ ,  $\frac{0.0333 - x}{x^2} = 1.6 \times 10^8$

$x_{\text{B}^{2+}} = 1.44 \times 10^{-5}\text{ M}$

$\text{pB}^{2+} = 4.84$



7. [16 pts] Derive the titration curve of 50.00 mL of 0.0200 M a monoprotic acid (HA,  $pK_a=6.00$ ) with 0.00 mL, 5.00 mL, 10.00 mL, and 15.00 mL of 0.1000 M KOH. Draw your calculated titration curve by indicating each point in the curve and indicate the equivalence point and  $pK_a$  in your graph (Note: label your x and y axes with units).



$$\textcircled{2} \quad \frac{50.00 \times 0.02}{0.1000} = 10 \text{ mL of KOH needed @ EP}$$

$$\textcircled{2} \quad 0.00 \text{ mL (Initial)}$$

$$[H^+] = \sqrt{K_a \cdot C_a} = \sqrt{10^{-6} \cdot 0.02} = 1.41 \times 10^{-4}$$

$$pH = 3.85$$

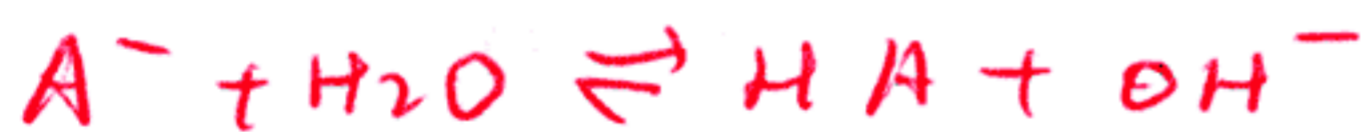
$\textcircled{2}$  5.00 (Before EP)

$$[HA] = \frac{50.00 \times 0.0200 - 5.00 \times 0.1000}{50.00 + 5.00} = 0.0091 \text{ M}$$

$$[A^-] = \frac{5.00 \times 0.1000 \text{ M}}{50.00 + 5.00} = 0.0091 \text{ M}$$

$$[H^+] = K_a \cdot \frac{[HA]}{[A^-]} = 10^{-6} \quad pH = 6.00$$

$\textcircled{2}$  10.00 (EP)



$$[OH^-] = \sqrt{K_b \cdot C_b} = \sqrt{\frac{K_w}{K_a} \cdot \left[ \frac{0.0200 \times 50.00}{(50.00 + 10.00)} \right]} = \sqrt{10^{-8} \cdot 0.0167} = 1.29 \times 10^{-5}$$

$$pH = 9.11$$

$\textcircled{2}$  15.00 (After EP)

$$[OH^-] = \frac{15.00 \times 0.1000 - 50 \times 0.0200}{50.00 + 15.00} = 0.0077 \text{ M}$$

$$pH = 11.89$$

