

Review Worksheet for Exam 3

1] What is the pH of a solution made by the mixing of 20.00 mL of 0.100 M HClO ($K_a = 2.96e-8$) with 12.00 mL of 0.100 M NaOH?



$$\text{Initial mol HClO} = 20.00 \text{ mL} * 0.100 \text{ M} = 2.00 \text{ mmol}$$

$$\text{Added mol OH}^- = 12.00 \text{ mL} * 0.100 \text{ M} = 1.20 \text{ mmol}$$

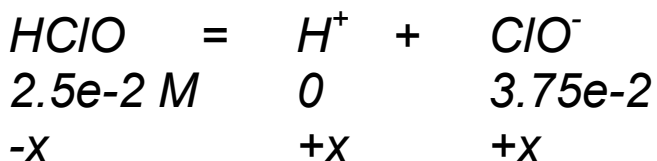
Excess HClO region also ClO⁻ makes a buffer



$$\text{Excess HClO} = 2.00 - 1.20 \text{ mmol} = 0.80 \text{ mmol}$$

$$[\text{HClO}] = 0.80 \text{ mmol} / 32.00 \text{ mL} = 2.5e-2 \text{ M}$$

$$[\text{ClO}^-] = 1.20 \text{ mmol} / 32.00 \text{ mL} = 3.75e-2 \text{ M}$$



$$x(3.75e-2 + x) / (2.5e-2 - x) = 2.96e-8$$

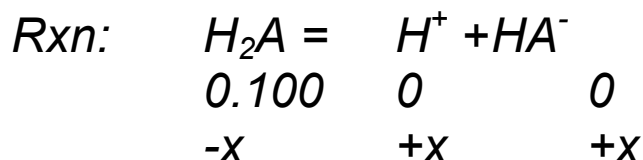
$$x = 2.0e-8 \text{ M}$$

$$\text{pH} = 7.70$$

2] 50.00 mL of 0.100 M H₂A is titrated with 0.100 M NaOH.

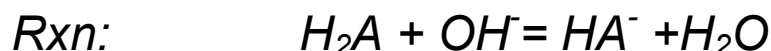
$$K_{a1} = 1.0e-3 \quad K_{a2} = 1.0e-7$$

a) Calculate pH when 0.00 mL of 0.100 M NaOH is added.



$$K_{a1} = 1.0e-3 = x^2 / (0.100-x) \quad x = 0.01 \quad pH = 2.00$$

b) 10.00 mL of 0.100 M NaOH



both H₂A and HA⁻ present, this is the buffer region

$$\text{initial } H_2A = 50.00 \text{ mL} * 0.100 \text{ M} = 5.00 \text{ mmol}$$

$$\text{added } OH^- = 10.00 \text{ mL} * 0.100 \text{ M} = 1.00 \text{ mmol}$$

$$[HA^-] = 1.00 \text{ mmol} / 60.00 \text{ mL} = 1.67e-2 \text{ M}$$

$$[H_2A] = 5.00 - 1.00 \text{ mmol} / 60.00 \text{ mL} = 6.67e-2 \text{ M}$$

$$K_{a1} = 1.0e-3 = [H^+][1.67e-2] / [6.67e-2]$$

$$[H^+] = 4.0e-3 \text{ M} \quad pH = 2.40$$

c) 50.00 mL of 0.100 M NaOH added.

$$\text{initial } H_2A = 50.00 \text{ mL} * 0.100 \text{ M} = 5.00 \text{ mmol}$$

$$\text{added } OH^- = 50.00 \text{ mL} * 0.100 \text{ M} = 5.00 \text{ mmol}$$

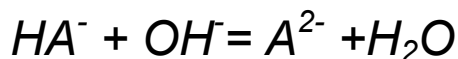
1st eq. pt. only HA⁻ remains

$$pH \approx \frac{1}{2} (pK_{a1} + pK_{a2}) = \frac{1}{2} (3.00 + 7.00) = 5.00$$

d) 60.00 mL of 0.100 M NaOH added.

$$\text{initial } H_2A = 50.00 \text{ mL} * 0.100 \text{ M} = 5.00 \text{ mmol}$$

$$\text{added } OH^- = 60.00 \text{ mL} * 0.100 \text{ M} = 6.00 \text{ mmol}$$



Second base is being neutralized

$$[A^{2-}] = 1.00 \text{ mmol} / 110.0 \text{ mL} = 9.09e-3 \text{ M}$$

$$[HA^-] = 4.00 \text{ mmol} / 110.0 \text{ mL} = 3.64e-2 \text{ M}$$

$$K_{a2} = 1.0e-7 = [H^+][9.09e-3] / [3.64e-2]$$

$$[H^+] = 4.0e-7 \quad pH = 6.40$$

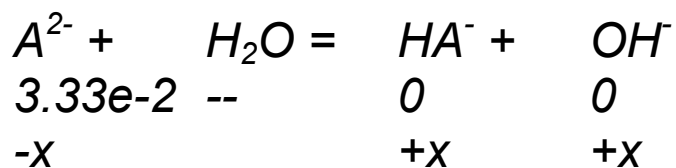
e) 100.00 mL of 0.100 M NaOH added.

$$\text{initial } H_2A = 50.00 \text{ mL} * 0.100 \text{ M} = 5.00 \text{ mmol}$$

$$\text{added } OH^- = 100.00 \text{ mL} * 0.100 \text{ M} = 10.00 \text{ mmol}$$

2nd eq. pt.

$$[A^{2-}] = 5.00 \text{ mmol} / 150.00 \text{ mL} = 3.33e-2 \text{ M}$$



$$K_b = K_w / K_{a2} = 1.00e-14 / 1.0e-7 = x^2 / (3.33e-2 - x)$$

$$x = 5.77e-5 \text{ M}$$

$$pOH = 4.239$$

$$pH = 9.76$$

3] 50 mL of 0.010 M Zn^{2+} is titrated with 0.010 M EDTA in 0.010 M NH_3 at pH 9.00.

a) calculate K_f'' .

Appendix I in your text has

$\log \beta_1 = 2.18$	$\beta_1 = 151$
$\log \beta_2 = 4.43$	$\beta_2 = 2.69e4$
$\log \beta_3 = 6.74$	$\beta_3 = 5.50e6$
$\log \beta_4 = 8.70$	$\beta_4 = 5.01e8$

$$\alpha_M = 1 / \{1 + \beta_1[L] + \beta_2[L]^2 + \dots + \beta_n[L]^n\}$$

$$\alpha_{\text{Zn}^{2+}} = 1 / \{1 + 151[0.010] + 2.69e4[0.010]^2 + 5.50e6[0.010]^3 + 5.01e8[0.010]^4\}$$

$$\begin{aligned} \alpha_{\text{Zn}^{2+}} &= 1 / \{1 + 1.51 + 2.69 + 550.0 + 5010.0\} \\ &= 1.79e-4 \end{aligned}$$

$$K_f = 3.2e16 \quad \text{Table 13-2}$$

$$\alpha_{\text{Y}^{4-}} = 5.4e-2 \quad \text{Table 13-1}$$

$$K_f'' = K_f \alpha_{\text{Zn}^{2+}} \alpha_{\text{Y}^{4-}} = 3.2e16 * 5.4e-2 * 1.79e-4 = 3.1e11$$

b) Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 25.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

$$\text{Initial } Zn^{2+} = 50.0 \text{ mL} * 0.0100 \text{ M} = 0.500 \text{ mmol}$$

$$\text{Added EDTA} = 25.0 \text{ mL} * 0.0100 \text{ M} = 0.250 \text{ mmol}$$

$$\text{Excess } Zn^{2+} = 0.500 - 0.250 = 0.250 \text{ mmol}$$

$$C_{Zn^{2+}} = 0.250 \text{ mmol} / 75.0 \text{ mL} = 3.33e-3 \text{ M}$$

$$[Zn^{2+}] = \alpha_{Zn^{2+}} C_{Zn^{2+}} = 1.79e-4 * 3.33e-3 \text{ M}$$

$$pZn = 6.225$$

c) Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 50.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

$$\text{Initial } Zn^{2+} = 50.0 \text{ mL} * 0.0100 \text{ M} = 0.500 \text{ mmol}$$

$$\text{Added EDTA} = 50.0 \text{ mL} * 0.0100 \text{ M} = 0.500 \text{ mmol}$$

$$\text{Initial } Zn^{2+} = \text{Added EDTA} \therefore \text{eq. pt.}$$

$$\text{Initial } [ZnY^{2-}] = 0.500 \text{ mmol} / 100.0 \text{ mL} = 5.00e-3 \text{ M}$$

$$ZnY^{2-} = C_{Zn^{2+}} + EDTA$$

$$5.00e-3 \quad 0 \quad 0$$

$$-x \quad +x \quad +x$$

$$K_f'' = 3.1e11 = (5.00e-3 - x) / x^2 \quad x = C_{Zn^{2+}}$$

$$x = 1.27e-7 \text{ M}$$

$$[\text{Zn}^{2+}] = \alpha_{\text{Zn}^{2+}} C_{\text{Zn}^{2+}} = 1.79e-4 * 1.27e-7 \text{ M}$$

$$[\text{Zn}^{2+}] = 2.27e-11 \text{ M}$$

$$p\text{Zn} = 10.64$$

d) Calculate the pZn when 50.0 mL of 0.0100 M Zn^{2+} is added to 75.0 mL of 0.0100 M EDTA in 0.010 M NH_3 at pH 9.00.

$$\text{Initial } \text{Zn}^{2+} = 50.0 \text{ mL} * 0.0100 \text{ M} = 0.500 \text{ mmol}$$

$$\text{Added EDTA} = 75.0 \text{ mL} * 0.0100 \text{ M} = 0.750 \text{ mmol}$$

$$\text{Excess EDTA} = 0.250 \text{ mmol}$$

$$[\text{ZnY}^{2-}] = 0.500 \text{ mmol} / 125.0 \text{ mL} = 4.00e-3$$

$$[\text{EDTA}] = 0.250 \text{ mmol} / 125.0 \text{ mL} = 2.00e-3 \text{ M}$$

$$K_f'' = 3.1e11 = [\text{ZnY}^{2-}] / C_{\text{Zn}^{2+}} * [\text{EDTA}]$$

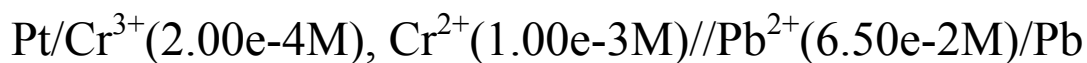
$$3.1e11 = 4.00e-3 / C_{\text{Zn}^{2+}} * 2.00e-3$$

$$C_{\text{Zn}^{2+}} = 6.45e-12$$

$$[\text{Zn}^{2+}] = \alpha_{\text{Zn}^{2+}} C_{\text{Zn}^{2+}} = 1.79e-4 * 6.45e-12 \text{ M} = 1.15e-15$$

$$p\text{Zn} = 14.94$$

4) Calculate E_{cell} and K for this reaction.



$$E_{\text{cath}} = -0.126 - (0.0592/2) \log 1/6.5\text{e-}2 = -0.161 \text{ V}$$

$$E_{\text{anod}} = -0.408 - 0.0592 \log (1.00\text{e-}3/2.00\text{e-}4) \\ = -0.449 \text{ V}$$

$$E_{\text{cell}} = -0.161 - (-0.449) = 0.288 \text{ V}$$

$$E^{\circ}_{\text{cell}} = -0.126 - (-0.408) = 0.282$$

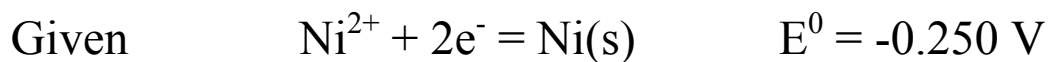
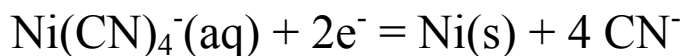
$$\Delta G^{\circ} = -nFE^{\circ} = -2*96484*0.282 = - 5.44\text{e}4 \text{ J}$$

$$\Delta G^{\circ} = -RT \ln K$$

$$\ln K = -\Delta G^{\circ} / RT = -(-5.44\text{e}4 \text{ J}) / 8.314 * 298\text{K}$$

$$K = 3.43\text{e}9$$

5) Calculate E^0 for



$$\beta \{ \text{Ni}(\text{CN})_4^- \} = 1.0\text{e}22$$

$$E = -0.250 - (0.0592/2) \log 1/[\text{Ni}^{2+}]$$

$$\beta \{ \text{Ni}(\text{CN})_4^- \} = 1.0\text{e}22 = [\text{Ni}(\text{CN})_4^-] / [\text{Ni}^{2+}][\text{CN}]^4$$

$$[\text{CN}]^4 1.0\text{e}22 / [\text{Ni}(\text{CN})_4^-] = 1/[\text{Ni}^{2+}]$$

$$E = -0.250 - (0.0592/2) \log \{ [\text{CN}]^4 1.0\text{e}22 / [\text{Ni}(\text{CN})_4^-] \}$$

$$E^0 = -0.250 - (0.0592/2) \log 1.0\text{e}22$$

$$E^0 = -0.90 \text{ V}$$

6) A cell potential was measured as 0.744 V versus the SCE. What would be the cell voltage if the SHE is used in place of the SCE? $E_{\text{SCE}} = 0.241$ volts

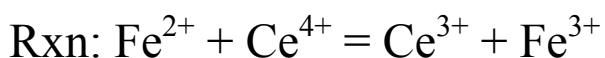
$$E_{\text{cell}} = E_{\text{cell}}(\text{SHE}) - E_{\text{SCE}}$$

$$0.744 = E_{\text{cell}}(\text{SHE}) - 0.241$$

$$E_{\text{cell}}(\text{SHE}) = 0.985 \text{ V}$$

7) Derive the titration curve for the titration of 50.00 mL of 0.0500 M Fe^{2+} with 0.100 M Ce^{4+} using these volumes of titrant:

- a) 5.00 mL of 0.100 M Ce^{4+}
- b) 25.00 mL
- c) 25.10 mL



a) 5.00 mL of 0.100 M Ce^{4+}

initial mol of $\text{Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M Fe}^{2+} = 2.50 \text{ mmol}$

added mol of $\text{Ce}^{4+} = 5.00 \text{ mL} * 0.100 \text{ M Ce}^{4+} = 0.500 \text{ mmol}$

$\text{Fe}^{2+} +$	$\text{Ce}^{4+} =$	$\text{Ce}^{3+} +$	Fe^{3+}
2.50	0.500	0	0
-0.500	-0.500	+0.500	+0.500
2.00	0	0.500	0.500

Both Fe^{2+} and Fe^{3+} are present this is a metal buffer.

$$E = 0.771 - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} = 0.771 - 0.0592 \log \frac{\frac{2.00 \text{ mmol}}{55.00 \text{ mL}}}{\frac{0.500}{55.00 \text{ mL}}}$$

$$E = 0.734 \text{ V}$$

b) 25.00 mL

initial mol of $\text{Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M Fe}^{2+} = 2.50 \text{ mmol}$

added mol of $\text{Ce}^{4+} = 25.00 \text{ mL} * 0.100 \text{ M Ce}^{4+} = 2.50 \text{ mmol}$

This is the equivalence point.

$$\begin{aligned} E &= E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]} \\ + E &= E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.0592 \log \frac{[\text{Fe}^{2+}]}{[\text{Fe}^{3+}]} \\ \hline 2E &= E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.0592 \log \frac{[\text{Fe}^{2+}][\text{Ce}^{3+}]}{[\text{Fe}^{3+}][\text{Ce}^{4+}]} \end{aligned}$$

Note that at the eq. pt. $[\text{Fe}^{2+}] = [\text{Ce}^{4+}]$ & $[\text{Fe}^{3+}] = [\text{Ce}^{3+}]$

Therefore

$$2E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 + E_{\text{Fe}^{3+}/\text{Fe}^{2+}}^0 - 0.0592 \log(1)$$

$$2E = 1.72 + 0.771$$

$$E = 1.25 \text{ V}$$

c) 25.1 mL of 0.100 M Ce^{4+}

initial mol of $\text{Fe}^{2+} = 50.00 \text{ mL} * 0.0500 \text{ M} \text{Fe}^{2+} = 2.50 \text{ mmol}$

added mol of $\text{Ce}^{4+} = 25.10 \text{ mL} * 0.100 \text{ M} \text{Ce}^{4+} = 2.51 \text{ mmol}$

Excess Ce^{4+} region

Fe^{2+}	+	Ce^{4+}	=	Ce^{3+}	+	Fe^{3+}
2.50		2.51		0		0
-2.50		-2.50		+2.50		+2.50
<hr/>						
0		0.01		2.50		2.50

$$E = E_{\text{Ce}^{4+}/\text{Ce}^{3+}}^0 - 0.0592 \log \frac{[\text{Ce}^{3+}]}{[\text{Ce}^{4+}]}$$

$$E = 1.72 - 0.0592 \log \frac{\frac{2.50 \text{ mmol}}{75.10 \text{ mL}}}{\frac{0.01 \text{ mmol}}{75.10 \text{ mL}}} = 1.58 \text{ V}$$