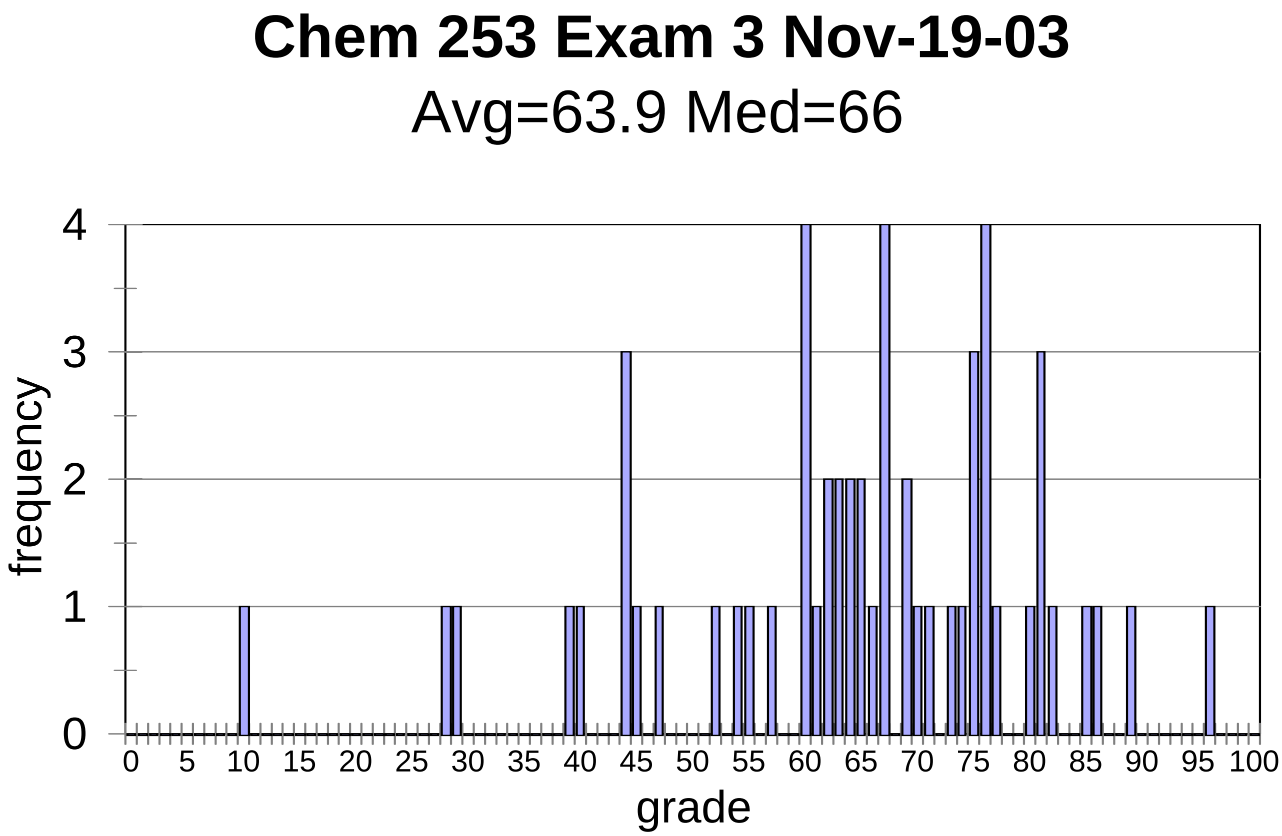
Chem 253 – Exam 3 – November 19, 2003

The answers are at the end of this exam.



100 total points.Questions 1-10 are worth 5 points each. Questions 11-15 are worth 10 points each.

1] Average of the homework problems _______________ (10 points)

The following questions are worth 5 points each.

2] Which of the following statements is true when we add 100.00 mL of 0.100 M $HClO_4$ to 50.0 mL of 0.100 M NaCN?

a) A buffer system is created by the presence of both HCN and CN^-
b) The conjugate base, CN^- is present and in greater concentration than HCN after the acid-base reaction.
c) pH = pK_a, where $K_a = [H^+][CN^-] / [HCN]$
d) pH = 1.48
e) pH = 7.00

3] The selection of a visual acid-base indicator should be based on __________________________.

a) its transition pH which should not overlap the steepest portion of the titration curve.
b) its transition pH which should overlap the excess H^+ portion of the titration curve.
c) its transition pH which should overlap the buffer portion of the titration curve.
d) its transition pH which should overlap the flattest portion of the titration curve.
e) its transition pH which should overlap the steepest portion of the titration curve.

4] The conditional formation constant K_f' for CaY^{2-} is related to K_f through which of the relationships?

a) $K_f' = K_f$ at pH =0
b) $K_f' = \alpha_{y4-} K_f$
c) $K_f = \alpha_{y4-} K_f'$
d) $K_f' = 1 / K_f$
e) $K_f' = K_f^2$

5] In reference to EDTA titrations the symbol, α_{y4-}, indicates which of the following?

a) The fraction of metal chelated by EDTA
b) The concentration of EDTA in the Y^{4-} form.
c) The fraction of EDTA in the Y^{4-} form.
d) The analytical concentration of metal.
e) The fraction of EDTA not in the Y^{4-} form.

6] A spontaneous electrochemical cell would have which of the following?

a) $E_{cell} = 0$
b) $E_{cell} > 0$
c) $E_{cell} < 0$
d) $E_{cell} \leq 0$
e) $E_{cell} \geq 0$

7] If A + e^- = B has E^0 = 0.775 V then the E^0 for 2A + $2e^-$ = 2B is ________________.

8] The standard cell potential for the following is

$Fe(s)/Fe^{2+}(aq)//Sn^{2+}(aq)/Sn(s)$	$Fe^{2+} + 2e^- = Fe(s)$	$E^0 = -0.44$ V
	$Sn^{2+} + 2e^- = Sn(s)$	$E^0 = -0.141$ V

a) –0.030
b) –0.581
c) 0.581
d) 0.44
e) 0.30

9] The E^0 for the following is

$FeCO_3(s) + 2e^- = Fe(s) + CO_3^{2-}$	$E^0 = ?$
$Fe^{2+} + 2e^- = Fe(s)$	$E^0 = -0.44$ V
K_{sp} {$FeCO_3(s)$} = 2.1e-11	

a) 0.756 V
b) –0.124 V
c) 0.124 V
d) –1.07
e) –0.756

10] It is advantageous to conduct EDTA titrations of metal ions in

a) acidic pH's to assist metal ion hydrolysis
b) basic pH's to prevent metal ion hydrolysis
c) basic pH's to maximize Y^{4-} fraction
d) basic pH's to minimize Y^{4-} fraction
e) acidic pH's to maximize Y^{4-} fraction

11] Which is true of the equivalence point for the redox titration of Fe^{2+} with Ce^{4+}?

a) only $[Fe^{2+}] = [Fe^{3+}]$
b) $[Fe^{2+}] = [Ce^{3+}]$ and $[Ce^{4+}] = [Fe^{3+}]$
c) $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$
d) $[Fe^{2+}] = [Fe^{3+}]$ and $[Ce^{4+}] = [Ce^{3+}]$
e) $[Fe^{2+}] = 0$

12] A pH electrode was found to have a potential of 0.241 V in a pH 4.01 buffer solution. A sample solution was found to have a potential of 0.252 V. What is the pH of that sample? E = const – 0.0592 pH

a) 3.82
b) 7.19
c) 7.04
d) 6.94
e) 10.11

13] $KMnO_4$ can be standardized with which of the following?

a) H_2O_2
b) CH_4
c) H_2O
d) NaC_2O_4
e) C_2H_4

The following questions are worth 10 points each

Table 13-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and $\mu = 0.10$ M

pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 13-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 ($\mu = 0.2$)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, $\mu = 0.2$)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 ($\mu = 0$)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 ($\mu = 1.0$)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, $\mu = 1.0$)
Cr^{3+}	23.4				

14] Calculate pCa if 20.0 mL of 0.050 M of EDTA is added to 15.0 mL of 0.050 M Ca^{2+} at pH 9.0.

15] Calculate the cell potential when 25.0 mL of 0.010 M Ce^{4+} is added to 15.0 mL of 0.010 M Fe^{2+}.

$Ce^{4+} + e^- = Ce^{3+}$	**$E^0 = 1.70$ V**
$Fe^{3+} + e^- = Fe^{2+}$	**$E^0 = 0.767$ V**

16] How many grams of $K_2C_2O_4$ (MW 166.22) must be added 25.0 mL of 0.500 M HCl to give a pH of 4.500 when this solution is diluted to 500.0 mL.

$K_{a1} = 5.60e{-2}$ $\quad$ $K_{a2} = 5.42e{-5}$

Answers

2] $[H^+]$ = 5.00 mmol / 150.0 mL = 3.33e-2 pH = 1.48

3] its transition pH which should overlap the steepest portion of the titration curve.

4] $K_f' = \alpha_{y4-}K_f$

5] The fraction of EDTA in the Y^{4-} form.

6] $E_{cell} > 0$

7] 0.775 V

8] E = -0.141 –(-0.44) = 0.30 V

9] E = -0.44 – (0.0592/2) log $1/K_{sp}$ = -0.756 V

10] basic pH's to maximize Y^{4-} fraction

11] $[Fe^{2+}] = [Ce^{4+}]$ and $[Fe^{3+}] = [Ce^{3+}]$

12] 3.82

13] NaC_2O_4

14] mol EDTA = 20.0 mL * 0.050 M = 1.0 mmol
mol Ca^{2+} = 15.0 mL * 0.050 M = 0.75 mmol

excess EDTA region where,

$[CaY^{2-}]$ = 0.75 mmol / 35.0 mL = 2.1e-2 M
[EDTA] = 0.25 mmol / 35.0 mL = 7.1e-3 M

$K_f = [CaY^{2-}] / [Ca^{2+}]*[Y^{4-}]$

$[Y^{4-}] = \alpha_{Y4-}$ [EDTA]

$K_f * \alpha_{Y4-} = K_f' = [CaY^{2-}] / [Ca^{2+}]*[EDTA]$

$K_f = 4.9e10$ $K_f' = 5.4e-2*4.9e10 = 2.6e9$

$2.6e9 = 2.1e-2\ M / [Ca^{2+}]*7.1e-3\ M$ $[Ca^{2+}] = 1.1e-9\ M$ pCa = 8.94

15] Mol Ce^{4+} = 25.0 mL * 0.010 M = 0.25 mmol
Mol Fe^{2+} = 15.0 mL * 0.010 M = 0.15 mmol

Excess Ce^{4+} region

Ce^{4+} +	Fe^{2+} =	Fe^{3+} +	Ce^{3+}
0.25	0.15	0	0
-0.15	-0.15	+0.15	+0.15
0.10	0	0.15	0.15

E = 1.70 – (0.0592) log (0.15/0.10) = 1.69 V

16] $pK_{a1} = 1.25$ $pK_{a2} = 4.27$

Therefore only K_{a2} is important. $HC_2O_4^- = H^+ + C_2O_4^{2-}$

$[C_2O_4^{2-}]_i = x / 0.500\ L$

$[H^+]_i$ = 25.0*0.500 mmol / 500.0 mL = 0.025 M

$[H^+]_f = 10^{-4.500} = 3.16e-5\ M$

x = mol $C_2O_4^{2-}$

H^+ +	$C_2O_4^{2-}$ =	$HC_2O_4^-$
0.025	x / 0.500L	0
-y	-y	+y
3.16e-5		

0.025 – y = 3.16e-5 y = 0.025 M

$K_a = [H^+][C_2O_4^{2-}] / [HC_2O_4^-]$

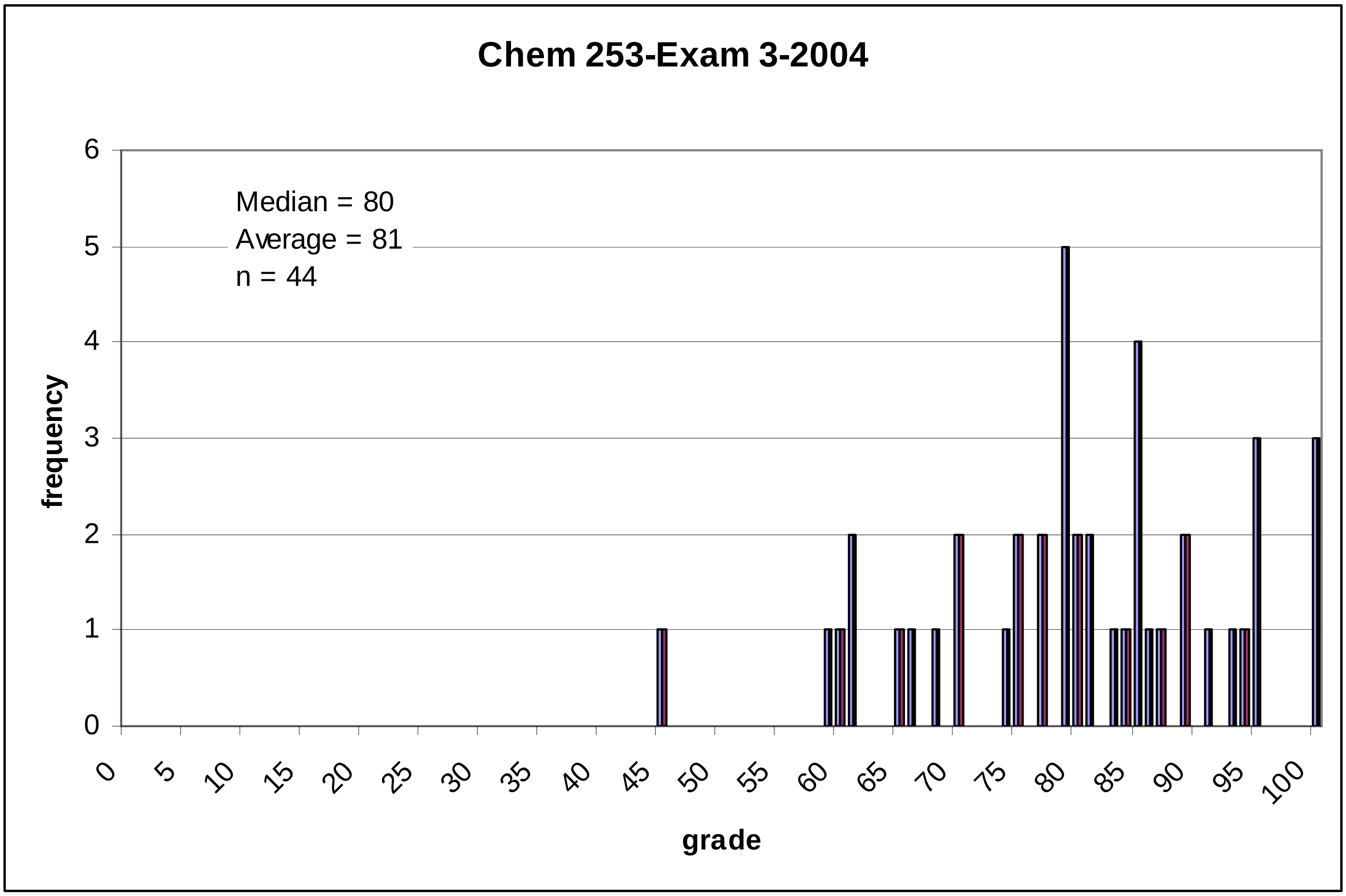
$5.42e-5 = [3.16e-5][C_2O_4^{2-}] / [0.025]$

$[C_2O_4^{2-}] = 4.29e-2\ M$

4.29e-2 M = x / 0.500L – 3.16e-5

x = 2.15e-2 mol

g $K_2C_2O_4$ = 2.15e-2 mol * 166.22 g/mol = 3.57 g


Chem 253-Exam 3-2004
Median = 80
Average = 81
n = 44
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grade

Instructions: Please use the bubble sheet to fill in the answers for problems 1-16. You may keep the first three pages of this exam when you are done. The last sheet of the exam is to be turned in.

Problems 1-2 involve the following titration:

1] 75.0-mL of 0.100 M $CH_3COOH(aq)$ (pKa = 4.757) is titrated with 0.0500 M NaOH(aq). What is the volume of NaOH solution required to reach the equivalence point? (5 points)

a) 150-mL b) 75.0-mL c) 50.0-mL d) 100-mL e) 125-mL

2] What is the pH of the equivalence point in problem 1? (5 points)

a) 7.000 b) 6.569 c) 10.368 d) 7.889 e) 8.640

3] What is the final pH if solutions of 200.0-mL of 0.0500 M NaOH(aq) and 75.0-mL of 0.100 M $CH_3COOH(aq)$ are added together? (5 points)

a) 10.554 b) 2.345 c) 7.000 d) 11.959 e) 14.000

4] What is the difference between the end point and equivalence point for a monobasic- monoacid titration? (5 points)

a] The equivalence point is where mol acid = mol base and the end point is where indicator changes color.
b] The end point is where mol acid = mol base and the equivalence point is where indicator changes color.
c] There are no differences between the concepts of the end and equivalence points.
d] The equivalence point is where mol acid = mol base and the end point is where the pH is 14.

5] 50.0-mL of 0.0500 M oxalic acid ($H_2C_2O_4$, pk_{a1} = 1.252, pK_{a2} = 4.266) is titrated with 50.0-mL of 0.0500 M NaOH. What is the pH of that titrated solution? (5 points)

a) 7.00 b) 1.252 c) 2.759 d) 4.266 e) 8.667

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4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 13-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
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Mg^{2+}	8.79	Hf^{4+}	29.5 (μ = 0.2)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
→ Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, μ = 0.2)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 (μ = 0)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
→ Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 (μ = 1.0)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, μ = 1.0)
Cr^{3+}	23.4				

6] What is K_f' for $SrEDTA^{2-}$ at pH 11?

a) 0.85 b) $10^{8.73}$ c) 0.85×8.73 d) $0.85\times10^{8.73}$ e) 1.55e-14

7] The formal concentration of EDTA is 1.00 mM. What is the concentration of the Y^{4-} form at pH 4?

a) 1.00 mM b) $3.8\times10^{-9} \times 1.00$ mM c) 3.8×10^{-9} mM d) 0.85 mM e) $0.85\times10^{8.73}$

<u>Problems 8-11 involve the following titration.</u>

8] A solution of 50.0-mL of 1.00×10^{-3} M $NiCl_2$(aq)is titrated with 1.00×10^{-3} M EDTA in a solution of 0.100 M NH_3 at pH 11.00. What is pNi if 25.0-mL of the titrant solution is added? Note that $\alpha_{Ni2+} = 1.34\times10^{-4}$ at 0.100 M NH_3. (5 points)

a) 7.350 b) 8.442 c) 5.311 d) 10.673 e) 11.995

9] What is K_f'' for the $NiEDTA^{2-}$ complex in 0.100 NH_3 at pH 11? (5 points)

a) $1.34\times10^{-4}(0.85)18.62$

b) $1.34\times10^{-4} \times 10^{18.62}$

c) $(0.85)10^{18.62}$

d) $1.34\times10^{-4}(0.85)10^{18.62}$

10] What is $[NiEDTA^{2-}]$ if 75.0-mL of titrant is added to the $NiCl_2$ solution in problem 8? (5 points)

a) 2.00e2 b) 5.23e-6 c) 2.00e-9 d) 7.99e-4 e) 4.00e-4

11] Which is true if 75.0-mL of 1.00×10^{-3} M EDTA titrant is added to the 50.0-mL of 1.00×10^{-3} M $NiCl_2$ solution in 0.1M NH_3? Assume equilibrium conditions. (5 points)

a) $[Ni^{2+}] = [EDTA]$

b) $[NiEDTA^{2-}] > [EDTA]$

c) $[NiEDTA^{2-}] = [EDTA]$

d) $[Ni^{2+}] > [EDTA]$

12] An electrochemical cell will discharge spontaneously if (5 points)

a) $E_{cell} < 0$

b) $E_{cell} > 0$

c) $E_{cell} = 0$

d) does not depend on E_{cell}

13] The reductions take place at which electrode? (5 points)

a) anode

b) toade

c) cathode

d) alkaline

e) amphiprotic

14] The purpose of a reference electrode is to provide (5 points)

a) to prevent mixing of the electrolyte solution.

b) to provide a means of ionic transport between the anode and cathode

c) to enable the reductive process at the anode.

d) to provide a stable potential in which an electrode reaction can be compared to.

e) to provide comic relief.

15] What is E^0_{cell} for the reaction below? (5 points)

$F_2 + 2Fe^{2+} = 2F^- + 2Fe^{3+}$

$F_2 + 2e^- = 2F^-$ $\quad E^0_{red} = 2.890$ V

$Fe^{3+} + e^- = Fe^{2+}$ $\quad E^0_{red} = 0.771$ V

a) -2.119 V

b) -1.348 V

c) 1.348 V

d) 0.655 V

e) 2.119 V

16] What is E^0_{cell} for the reaction below? (5 points)

$Hg_2SO_4(s) + 2e- = 2Hg(l) + SO_4^{2-}$

$Hg_2^{2+} + 2e^- = 2Hg(l)$ $\quad E^0_{red} = 0.796$ V

$Hg_2SO_4(s) = Hg_2^{2+} + SO_4^{2-}$ $\quad K_{sp} = 7.4e-7$

a) $E^0_{cell} = 0.796 - \frac{0.0592}{2}\log\frac{1}{K_{sp}}$

b) $E^0_{cell} = 0.796 - \frac{0.0592}{2}\log K_{sp}$

c) $E^0_{cell} = 0.796 - 0.0592\log\frac{1}{K_{sp}}$

d) $E^0_{cell} = 0.796 - \log\frac{1}{K_{sp}}$

17] What are the final concentrations of each ion when 25.0-mL of 0.0500 M Ce^{4+} is mixed with 15.0-mL of 0.0500 M Cu^+? (5 points)

$Ce^{4+} + e = Ce^{3+}$ $E^0_{red} = 1.44$ V
$Cu^{2+} + e = Cu^+$ $E^0_{red} = 0.161$ V

18] What is the potential of the final solution when 25.0-mL of 0.0500 M Ce^{4+} is mixed with 15.0-mL of 0.0500 M Cu^+? (5 points)

Homework Average = ________________________
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Answers

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1 & 2] eq. pt. mol CH_3COOH = mol OH^-

mol CH_3COOH = 75.0-mL*0.100 M = 7.50 mmol
vol NaOH = 7.50 mmol/0.0500 M = 150-mL

total volume = 150-mL+75.0-mL = 225-mL

$[CH_3COO^-]$ = 7.50 mmol/225-mL = 3.33e-2 M

CH_3COO^-	+	H_2O	=	CH_3COOH	+	OH^-
3.33e-2		--		0		0
- x		--		+ x		+ x

$K_b = K_w/K_a = 5.71e-10 = x^2/(3.33e-2-x) \approx x^2/(3.33e-2)$

x = 4.36e-6 pOH = 5.360 **pH =8.640**

3] mol CH_3COOH = 75.0-mL*0.100 M = 7.50 mmol
mol OH^- = 200.0-mL*0.0500 M = 10.0 mmmol

excess OH- = 10.0 – 7.50 mmol = 2.50 mmol
$[OH^-]$ = 2.50 mmol/275-mL = 9.09e-3
pOH = 2.041
pH = 11.959

4] a] The equivalence point is where mol acid = mol base and the end point is where indicator changes color.

5] mol of OH^- = 50.0-mL*0.0500 M = 2.50 mmol
mol of $H_2C_2O_4$ = 50.0-mL*0.0500 M = 2.50 mmol

Therefore we have only $HC_2O_4^-$ which is an amphiprotic species. pH is

$pH = ½(pk_{a1} + pK_{a2})$ **= ½(4.266 + 1.252) = 2.759**

6] $K_f' = \alpha_{y4-}K_f = 0.85*5.4e8 = 4.6e8$

7] [**Y^{4-}**] = 3.8e-9*1.00e-3 M = 3.8e-12 M b and c are correct.

8] Initial mol Ni^{2+} = 50.0-mL*1.00e-3 M = 0.0500 mmol
Added mol EDTA = 25.0-mL*1.00e-3 M = 0.0250 mmol

Excess Ni^{2+} = 0.0500 – 0.0250 mmol = 0.0250 mmol

C_{Ni2+} = 0.0250 mmol / 75.0-mL = 3.33e-4 M

Free [Ni^{2+}] = α_{Ni2+} C_{Ni2+} = 1.34e-4*3.33e-4 = 4.47e-8 M **pNi = 7.350**

9] $K_f'' = \alpha_{Ni2+}\alpha_{Y4-}*K_f$ **=** $1.34e-4*0.85*10^{18.62}$ **= 4.7e14**

10&11]Initial mol Ni^{2+} = 50.0-mL*1.00e-3 M = 0.0500 mmol
Added mol EDTA = 75.0-mL*1.00e-3 M = 0.0750 mmol

[NiEDTA] = 0.0500 mmol / 125.0-mL = 4.00e-4 M

Excess EDTA = 0.0250 mmol / 125.0-mL = 2.00e-4 M

Kf'' = [NiEDTA]/C_{Ni}*[EDTA] = 4.00e-4/C_{Ni}*2.00e-4 = 4.7e14

C_{Ni} = 4.3e-15 [Ni^{2+}] = 1.34e-4*4.3e-14 = 5.8e-18 M **pNi = 17.24**

Therefore [$NiEDTA^{2-}$] > **[EDTA]**

12] b) $E_{cell} > 0$

13] cathode

14] d) to provide a stable potential in which the cathode reaction can be compared.

15] Ecell = Ecath – Eanod = 2.890 – 0.771 = **2.119 V**

16] $E = 0.796 – 0.0592/2 \log 1/[Hg_2^{2+}]$

$K_{sp} = 7.4e-7 = [Hg_2^{2+}][SO_4^{2-}]$
$[Hg_2^{2+}] = 7.4e-7/[SO_4^{2-}]$

$E = 0.796 – 0.0592/2 \log [SO_4^{2-}]/7.4e-7 =$ **0.615 V**

17&18] Reaction: $Ce^{4+} + Cu^{+} = Ce^{3+} + Cu^{2+}$

Initial mol Ce^{4+} = 25.0-mL*0.0500 M = 1.25 mmol
Initial mol Cu^{+} = 15.0-mL*0.0500 M = 0.75 mmol

More Ce^{4+} than Cu^{+} therefore

Mol Ce^{3+} = 0.75 mmol	[Ce^{3+}] = 0.75 mmol / 40.0-mL = 1.9e-2 M
Mol Ce^{4+} = 0.50 mmol	[Ce^{4+}] = 0.50 mmol / 40.0-mL = 1.3e-2 M
Mol Cu^{+} = 0.00 mmol	[Cu^{+}] = 0.00
Mol Cu^{2+} = 0.75 mmol	[Cu^{2+}] = 0.75 mmol / 40.0-mL = 1.9e-2 M

E = 1.44 – 0.0592 log 1.9e-2 / 1.3e-2 = 1.43 V

Chem 253 – Exam 3 – November 16, 2005

Instructions

- **Do not start this exam until you are instructed to do so.**
- Problems 1-18 are worth 5 points each.
- Use the Scantron sheet to fill in the answers.
- Be sure to write your name on the Scantron sheet.
- You may take questions 1-18 with you when you done with the exam.
- Problem 19 must be turned in when you leave this room.

Table 13-1 Values of $\alpha_{Y^{4-}}$ for EDTA at 20°C and μ = 0.10 M

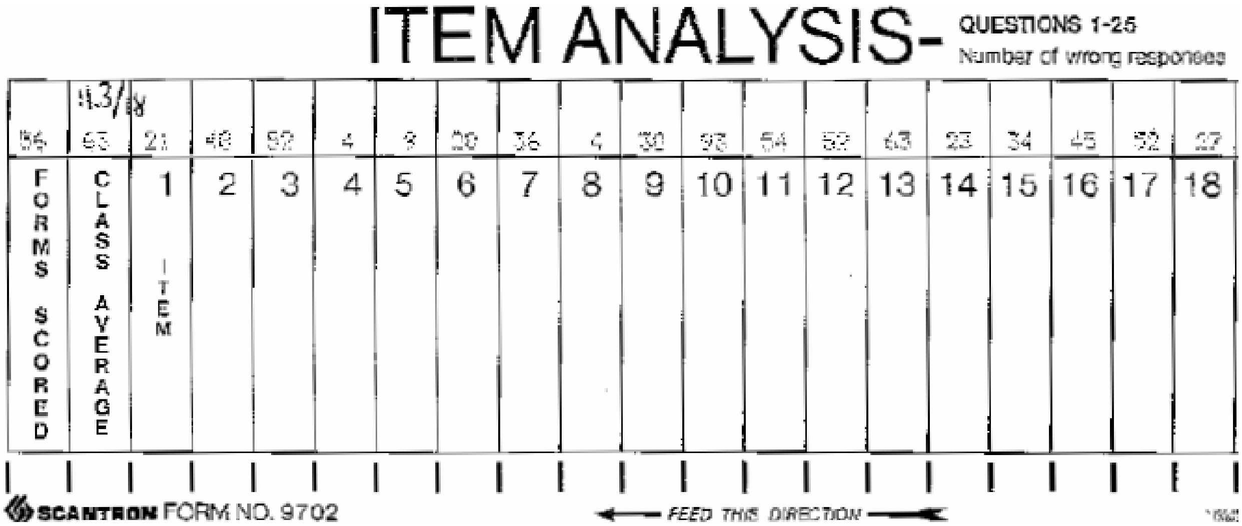
pH	$\alpha_{Y^{4-}}$
0	1.3×10^{-23}
1	1.9×10^{-18}
2	3.3×10^{-14}
3	2.6×10^{-11}
4	3.8×10^{-9}
5	3.7×10^{-7}
6	2.3×10^{-5}
7	5.0×10^{-4}
8	5.6×10^{-3}
9	5.4×10^{-2}
10	0.36
11	0.85
12	0.98
13	1.00
14	1.00

Table 13-2 Formation constants for metal-EDTA complexes

Ion	log K_f	Ion	log K_f	Ion	log K_f
Li^+	2.79	Mn^{3+}	25.3 (25°C)	Ce^{3+}	15.98
Na^+	1.66	Fe^{3+}	25.1	Pr^{3+}	16.40
K^+	0.8	Co^{3+}	41.4 (25°C)	Nd^{3+}	16.61
Be^{2+}	9.2	Zr^{4+}	29.5	Pm^{3+}	17.0
Mg^{2+}	8.79	Hf^{4+}	29.5 (μ = 0.2)	Sm^{3+}	17.14
Ca^{2+}	10.69	VO^{2+}	18.8	Eu^{3+}	17.35
Sr^{2+}	8.73	VO_2^+	15.55	Gd^{3+}	17.37
Ba^{2+}	7.86	Ag^+	7.32	Tb^{3+}	17.93
Ra^{2+}	7.1	Tl^+	6.54	Dy^{3+}	18.30
Sc^{3+}	23.1	Pd^{2+}	18.5 (25°C, μ = 0.2)	Ho^{3+}	18.62
Y^{3+}	18.09			Er^{3+}	18.85
La^{3+}	15.50	Zn^{2+}	16.50	Tm^{3+}	19.32
V^{2+}	12.7	Cd^{2+}	16.46	Yb^{3+}	19.51
Cr^{2+}	13.6	Hg^{2+}	21.7	Lu^{3+}	19.83
Mn^{2+}	13.87	Sn^{2+}	18.3 (μ = 0)	Am^{3+}	17.8 (25°C)
Fe^{2+}	14.32	Pb^{2+}	18.04	Cm^{3+}	18.1 (25°C)
Co^{2+}	16.31	Al^{3+}	16.3	Bk^{3+}	18.5 (25°C)
Ni^{2+}	18.62	Ga^{3+}	20.3	Cf^{3+}	18.7 (25°C)
Cu^{2+}	18.80	In^{3+}	25.0	Th^{4+}	23.2
Ti^{3+}	21.3 (25°C)	Tl^{3+}	37.8 (μ = 1.0)	U^{4+}	25.8
V^{3+}	26.0	Bi^{3+}	27.8	Np^{4+}	24.6 (25°C, μ = 1.0)
Cr^{3+}	23.4				

Table 14-1 Ordered redox potentials

Oxidizing agent ⇌ Reducing agent	$E°$ (V)
$F_2(g) + 2e^- \rightleftharpoons 2F^-$	2.890
$O_3(g) + 2H^+ + 2e^- \rightleftharpoons O_2(g) + H_2O$	2.075
⋮	
$MnO_4^- + 8H^+ + 5e^- \rightleftharpoons Mn^{2+} + 4H_2O$	1.507
⋮	
$Ag^+ + e^- \rightleftharpoons Ag(s)$	0.799
⋮	
$Cu^{2+} + 2e^- \rightleftharpoons Cu(s)$	0.339
⋮	
$2H^+ + 2e^- \rightleftharpoons H_2(g)$	0.000
⋮	
$Cd^{2+} + 2e^- \rightleftharpoons Cd(s)$	−0.402
⋮	
$K^+ + e^- \rightleftharpoons K(s)$	−2.936
$Li^+ + e^- \rightleftharpoons Li(s)$	−3.040



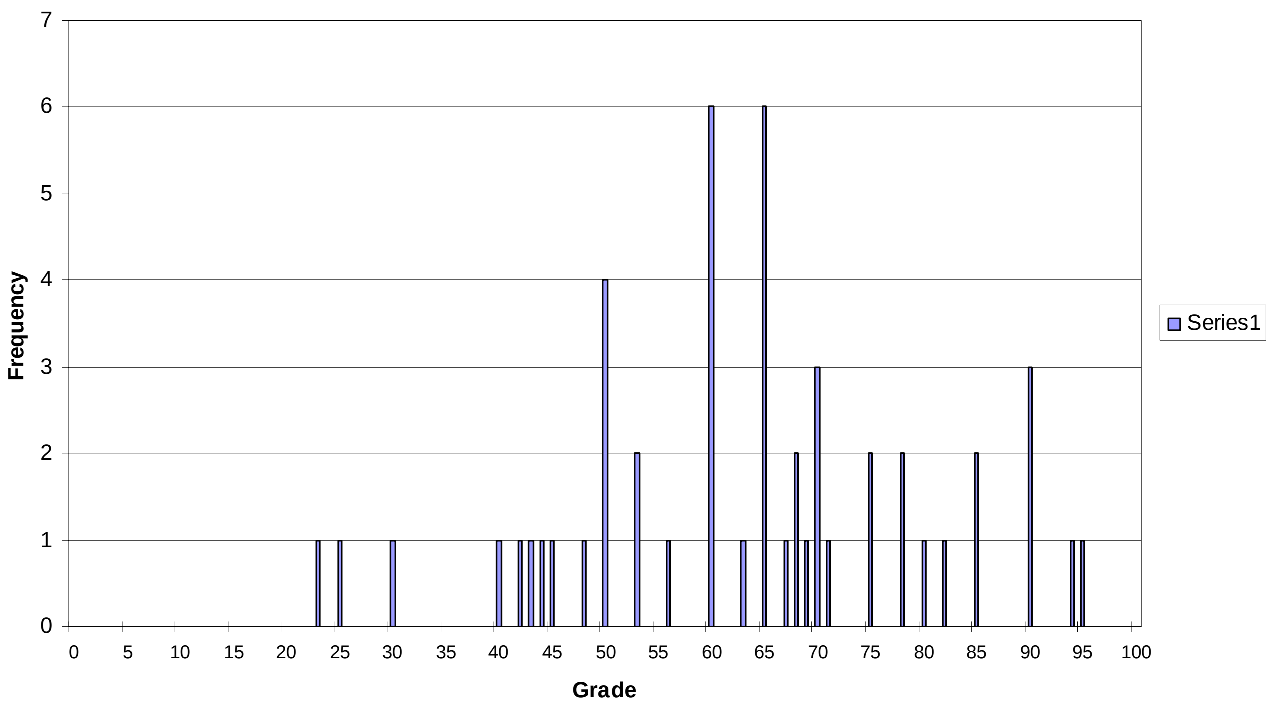
ITEM ANALYSIS- QUESTIONS 1-25

Number of wrong responses

FORMS SCORED	CLASS AVERAGE	ITEM 1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
56	63 (63/.8)	21	48	52	4	9	20	36	4	30	93	54	52	63	23	34	45	52	27

SCANTRON FORM NO. 9702 ← FEED THIS DIRECTION ←

Chem 253 Exam 3 2005 Avg 63 Med 65



1] When titrating a weak acid with a strong base it is expected that the equivalence point will be

a) Slightly acidic, since the equilibrium HA Ý H^+ + A^- predominates.
b) Neutral since $[OH^-] = [H^+]$
c) Slightly basic since the equilibrium A^- + H_2O Ý HA + OH^- predominates.
d) It is impossible to know since it could be acidic or basic depending on the K_a of the acid.
e) Strongly basic since excess OH^- is present.

2] A sample solution of 50.00 mL 0.0500 M oxalic acid ($H_2C_2O_4$) is titrated with 50.00 mL of 0.1000 M of NaOH. Which of the following is true after the two solutions are mixed?

a) This is the first equivalence point.
b) This a pH buffer region where $[H_2C_2O_4] = [HC_2O_4^-]$
c) This is a metal buffer region
d) This is the second equivalence point.
e) This is the excess OH^- region where the pH is strongly alkaline.

3] A sample solution of 50.00 mL 0.0500 M oxalic acid ($H_2C_2O_4$) is titrated with 35.00 mL of 0.1000 M of NaOH. Which of the following is true after the two solutions are mixed?

a) There is 2.50 mmol of $H_2C_2O_4$ present.
b) There is 1.50 mmol of OH^- present.
c) There is 2.50 mmol of $HC_2O_4^-$ present.
d) There is 1.00 mmol of $H_2C_2O_4$ present.
e) There is 1.00 mmol of $C_2O_4^{2-}$ present

4] What is the fraction of EDTA in the Y^{4-} form at pH 7.00?

a) 1.00
b) 5.0e-4
c) 0.36
d) 0.500
e) 3.3e-14

5] What is the conditional formation constant of $CaEDTA^{2-}$ at pH 10.00?

a) 1.8e10
b) 10.69
c) 32
d) 4.9e-10
e) 1.6e6

6] The fraction of free metal in the following equilibrium can be expressed as:

M + L Ý ML   É = [ML] / [M][L]

a) $\alpha_m = \frac{[M]}{1+\beta}$

b) $\alpha_m = \frac{[M]}{1+\beta[L]}$

c) $\alpha_m = \frac{1}{1+\beta[L]}$

d) $\alpha_m = \frac{1}{1+\beta[L]+\beta[L]^2}$

e) $\alpha_m = \frac{1}{1+\beta}$

7] What is the pH of a titration solution that consists of 0.100 M CH_3COOH (K_a = 1.75e-5) and 0.050 M NaOH?

a) 9.76
b) 5.81
c) 7.39
d) 4.81
e) 4.76

8] What is E^0 for the following half reaction if E^0 for Zn^{2+} + $2e^-$ Ý Zn(s) is -0.762 V?

½ Zn^{2+} + e^- Ý ½ Zn(s)

a) 0.762
b) – 0.381
c) 0.381
d) – 1.524
e) – 0.762

9] What is E^0_{cell} for the following reaction? 2Na(s) + $2H^+$ Ý $2Na^+$ + H_2(g)

Na^+ + e^- Ý Na(s) E^0 = - 2.7143 V
$2H^+$ + $2e^-$ Ý H_2(g) E^0 = 0.0000 V

a) 5.4286 V
b) -5.4286 V
c) -2.7143 V
d) 2.7143 V
e) 1.3572 V

10] What is the half reaction potential for reduction of 1.00e-5 M H^+?

a) 0.0000 V
b) 0.296 V
c) -0.296 V
d) 0.148 V
e) -0.148 V

11] The response of a F^- selective electrode was found to be 0.355 V in standardize 1.00e-3 M solution. The response of this electrode in an unknown solution of F^- is 0.407 V. What is $[F^-]$ for that unknown solution?

a) 1.05e-6 M
b) 2.33e-3 M
c) 1.30e-4 M
d) 7.13e-2 M
e) 5.55e-4 M

12] 18.00 mL of 0.125 M Sn^{4+} is titrated with 0.100 M Ti^{2+} in the following reaction:

$$Sn^{4+} + 2Ti^{2+} = Sn^{2+} + 2Ti^{3+}$$

What is the added volume of titrant required to reach the equivalence point?

a) 45.0 mL
b) 22.5 mL
c) 90.0 mL
d) 120.0 mL
e) 12.5 mL

13] Which of the following is true at the equivalence point of problem 12?

a) $[Sn^{4+}] = [Ti^{2+}]$ & $[Sn^{2+}] = [Ti^{3+}]$
b) $[Sn^{4+}] = [Ti^{2+}] = [Sn^{2+}] = [Ti^{3+}]$
c) $4[Sn^{4+}] = 2[Ti^{2+}]$ & $2[Sn^{2+}] = 3[Ti^{3+}]$
d) $2[Sn^{4+}] = [Ti^{2+}]$ & $2[Sn^{2+}] = [Ti^{3+}]$
e) $[Sn^{4+}] = 2[Ti^{2+}]$ & $[Sn^{2+}] = 2[Ti^{3+}]$

14] The linear pH range for the average pH electrode is about:

a) 0 to 14
b) -5 to 18
c) 2 to 10
d) 1 to 14
e) -10 to 10

15] A very common interference for the glass pH electrode is

a) F^-
b) Cl^-
c) Br^-
d) Na^+
e) C

16] Calculate the pH of a mixture of 25.00 mL of 0.500 M NaOH and 25.00 mL of 0.250 M H_3AsO_4 (arsenic acid).

$H_3AsO_4 = H_2AsO_4^- + H^+$ $K_{a1} = 5.8e\text{-}3$
$H_2AsO_4^- = HAsO_4^{2-} + H^+$ $K_{a2} = 1.10e\text{-}7$
$HAsO_4^{2-} = AsO_4^{3-} + H^+$ $K_{a3} = 3.2e\text{-}12$

a) 11.64
b) 9.23
c) 5.15
d) 1.68
e) 3.66

17] Which of the following species is the strongest reducing agent?

$A^+ + e^- = A$ $E^0 = 0.75$ V
$B + e^- = B^-$ $E^0 = 0.25$ V
$D^{2+} + e^- = D^+$ $E^0 = -0.50$ V

a) A^+
b) B^-
c) B
d) D^{2+}
e) D^+

18] Calculate the standard state cell potential for the following

$Cu(s)/Cu^{2+}(aq)//K^+(aq)/K(s)$

a) -3.275 V
b) 3.275 V
c) 2.587 V
d) -2.597 V
e) 1.881 V

Name: ____ Section Number: ________

19] What is the standard state reduction potential for the following reaction?

$AgBr(s) + e^- = Ag(s) + Br^-$

$Ag^+ + e^- = Ag(s)$ $E^0 = 0.799$ V
$AgBr(s) = Ag^+ + Br^-$ $K_{sp} = 5.0e-13$

Answers 1] c 2] d 3] e: 1.00 mmol past 1st eq. pt. Initial HA- = 2.5 mmol

HA^-	+	OH^-	=	A^{2-}	+	H_20	
2.50		1.00		0			
-1.00		-1.00		+1.00			
1.50		0		1.00			1.00 mmol A^{2-}

4] b 5] a: $K_f' = 0.36*10^{10.69} = 1.8e\text{-}10$ 6] c 7] e: pH = pKa

8] e 9] d: E^0_{cell} = 0.0000 – (-2.7143) V

10] c: $E = E^0 - 0.0592 \log 1/[H^+]$ = 0.0000 – 0.0592 log 1/[1.00e-5] = -0.296 V

11] c: E = const – 0.0592 log $[F^-]$
0.355 = const – 0.0592 log [1.00e-3]
const = 0.177

0.407 = 0.177 – 0.0592 log $[F^-]$ $[F^-]$ = 1.30e-4 M

12] a: 18.00 mL*0.125 M Sn^{4+}*(2mol Ti^{2+}/mol Sn^{4+})*1/0.100 M Ti^{2+} = 45.0 mL

13] d 14] c 15] d

16] b: 2nd eq. pt where all H_3AsO_4 is titrated to $HAsO_4^{2-}$ which is intermediate of $H_2AsO_4^-$ and AsO_4^{3-}. These two equilibria become important:

$H_2AsO_4^- = HAsO_4^{2-} + H^+$ K_{a2} = 1.10e-7
$HAsO_4^{2-} = AsO_4^{3-} + H^+$ K_{a3} = 3.2e-12

Therefore pH = ½($pK_{a2} + pK_{a3}$) = ½ (6.958<u>6</u> + 11.49<u>5</u>) = 9.23

17] e 18] a: $E_{cell} = E_{cath} - E_{anod}$ = -2.936 – 0.339 = -3.275 V

19] Start with: $E = E^0(Ag^+/Ag) - 0.0592 \log 1/[Ag^+]$

Realize that $K_{sp} = [Ag^+][Br^-]$ $[Ag^+] = K_{sp} / [Br^-]$ sub into Nernst Eqn above

$E = E^0(Ag^+/Ag) - 0.0592 \log [Br^-]/K_{sp}$ let [Br-] = 1 for standard state conditions

E^0 = 0.799 – 0.0592 log 1/5.00e-13 = 0.0708 V