Time: 2½ hours

Chemistry 206
Final Examination

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Calculators allowed
Periodic Tables Provided

Family Name: ____________________ First Name: ____________________

ID No. ______________________ Major: ____________________

Score:	
1	7
2	8
3	9
4	10
5	11
6	12
	13

Data:

Reaction	E°(Volts)
$Fe(CN)_6^{3-} + e^- = Fe(CN)_6^{4-}$	0.36
$AgBr(s) + e^- = Ag(s) + Br^-$	0.073
$Fe^{2+} + 2e^- = Fe(s)$	−0.440
$O_2(g) + 4H^+ + 4e^- = 2H_2O(l)$	1.229
$Cl_2 + 2e^- = 2Cl^-$	1.359
$V(OH)_4^+ + 2H^+ + e^- = VO^{2+} + 3H_2O$	1.00
$SO_4^{2-} + 4H^+ + 2e^- = H_2SO_3 + H_2O$	0.172
$Fe^{3+} + e^- = Fe^{2+}$	0.771
$Sn^{4+} + 2e^- = Sn^{2+}$	0.154

Ka's at 25°C

	Ka_1	Ka_2	Ka_3	Ka_4
H_3PO4	7.11×10^{-3}	6.32×10^{-8}	4.5×10^{-13}	–
H_4Y	1.02×10^{-2}	2.14×10^{-3}	6.92×10^{-7}	5.50×10^{-11}
$H_2C_4H_4O_6$	9.20×10^{-4}	4.31×10^{-5}	–	–

1. Consider the following oxidation-reduction reaction:

$$Fe(CN)_6^{3-} + Ag(s) + Br^- \longrightarrow Fe(CN)_6^{4-} + AgBr(s)$$

Which of the following statements is <u>incorrect</u> about this reaction?

a. The reaction is a spontaneous reaction as written.

b. $Fe(CN)_6^{3-}$ is the oxidizing agent.

c. $Fe(CN)_6^{3-}$ is a better electron acceptor than AgBr(s).

d. The equilibrium constant for the reaction is small.

e. The cell diagram for a galvanic cell with the above cell reaction to operate under standard conditions would be:
$Ag(s)|AgBr(sat'd),Br^-(1.00M)||Fe(CN)_6^{3-}(1.00M),Fe(CN)_6^{4-}(1.00M)|Pt$

2. Calculate the $[Cu^{2+}]$ in a solution that is:

a. 0.128M in NH_3 and 0.0250M in $Cu(NH_3)_4^{2+}$
The overall formation constant, β_4, for $Cu(NH_3)_4^{2+}$ is 5.62×10^{11}:

<u>Answer</u>: $[Cu^{2+}] =$

Give the defining reaction for β_4:

<u>Answer</u>:

b. 4.00×10^{-3} M in $Cu(NO_3)_2$, 2.90×10^{-2} M in Na_2H_2Y, and the pH is fixed at 4.00.
$K_{CuY} = 6.3 \times 10^{18}$, $\alpha_4 = 3.6 \times 10^{-9}$ at pH = 4.00.

<u>Answer</u>: $[Cu^{2+}] =$

c. Compute E° for the process

$$CuY^{2-} + 2e^- \rightleftharpoons Cu(s) + Y^{4-}$$
$E°_{Cu^{2+}/Cu} = 0.337$ volts

<u>Answer</u>: $E°_{CuY^{2-}} =$

3. Consider the half-cell: Pt, O_2 (780torr)|HCl (1.50×10^{-4} M):

Which of the following statements is correct for the galvanic cell that couples this half-cell with SHE?

a. The Nernst equation for the electrode potential is:

$$E_{O_2/O^{2-}} = 1.229 - \frac{0.0592}{4}\log\frac{1}{(750)(1.50\times10^{-4})^4}$$

b. The half-cell would act as anode when coupled with SHE in a galvanic cell.

c. The overall reaction for the galvanic cell would be:

$O_2(g) + 2H_2(g) \rightleftarrows 2H_2O(l)$

d. The cell potential will be equal to 1.157 volts.

e. $Cl_2(g)$ will form at the anode.

4. a. Give the expression (in terms of the reactant and product species concentrations) for the electrode potential E_{eq}, of the following reaction at the equivalence point:

$$2V(OH)_4^{+} + H_2SO_3 \rightleftarrows SO_4^{2-} + 2VO^{2+} + 5H_2O$$

Answer: E_{eq} =

b. Calculate the numerical value of E_{eq} in(a) for $[H^+] = 0.100$ M:

Answer: E_{eq} =

c. Give the general characteristics of a redox indicator that would be suitable to detect the equivalence point in a visual titration of the reaction in (a).

Answer:

5. You are asked to construct the titration curve for the titration:

50.00ml of 0.1000 M Fe^{3+} with 0.05000 M Sn^{2+}

a. Give the balanced titration reaction:

b. Calculate the volume of titrant at which E_{cell} for the titration cell

SHE || Fe^{3+}, Fe^{2+}, Sn^{2+}, Sn^{4+} | Pt equals $E^{\circ}_{Fe^{3+}/Fe^{2+}}$:

Answer: $V_{titrant} =$

c. Calculate the volume of titrant at which E_{cell} for the titration cell in (b) equals $E^{\circ}_{Sn^{4+}/Sn^{2+}}$:

Answer: $V_{titrant} =$

6. a. Give, in shorthand notation, an indicator electrode of the first kind for Hg(II):

Answer:

b. Give the Nernst equation for the E_{ind} in (a) as a function of pHg:

Answer:

c. Give, in shorthand notation, an indicator electrode of the second kind for EDTA:

Answer:

d. Give the half-cell reaction for the electrode in (c):

Answer:

e. Give the Nernst equation for E_{ind} in (c) as a function of pY:

Answer:

7. The following cell:
SCE || MgA_2 ($a_{Mg^{2-}}$ =9.62 x 10^{-3})/membrance electrode for Mg^{2+} has a potential of 0.367 volts. (A is an anion). When the solution of known magnesium activity is replaced with an unknown solution, the potential is 0.244 volts. Calculate the pMg of this unknown solution:

Answer:

8. Consider the titration of 50.00ml of 0.1000 M solution of ethylenediamine ($H_2NCH_2CH_2NH_2$,B) with a 0.2000 M solution of HCl. K_{b1} = 8.47 x 10^{-5} , K_{b2} = 7.04 x 10^{-8} for B:

a. Calculate the pH of the solution at V_{HCl} = 0ml:

Answer: pH =

b. Identify the system at V_{HCl} = 12.50mls: Specify concentration of each species that makes up the system:

Answer:

c. Calculate the pH of the solution at V_{HCl} = 12.50ml:

Answer: pH =

d. Identify the system at V_{HCl} = 25.00ml:

Answer:

e. What is the expression for $[H_3O^+]$ at V_{HCl} = 25.00ml:

Answer: $[H_3O^+]$ =

f. Calculate the pH at V_{HCl} = 25.00ml:

Answer:

g. Calculate the pH at V_{HCl} = 50.00ml:

Answer: pH =

13. a. A solution contains 1.694mg of $CoSO_4$ (155.0g mol^{-1}) per milliliter. Calculate the volume of 0.009450 M Zn^{2+} needed to titrate the excess reagent after addition of 50.00ml of 0.008640 M EDTA to a 25.00ml aliquot of this solution.

Answer: $V_{Zn^{2+}}$ =

b. Give two reasons (short statements) why multidentate ligands are preferable to unidentate ligands for complexometric titrations:

Answer:

c. Calculate the $[H_3O^+]$ in an aqueous solution of 0.0100 M Na_2H_2Y:

Answer:

9. a. Name and give the chemical formulas of two primary standards for standardization of acids:

b. Name and give the chemical formulas of two primary standards for standardization of bases:

10. a. Calculate the mass of KHP (204.22g mol^{-1}) needed to standardize a 0.0400 M NaOH solution if $V_{titrant}$ should be 30.00ml.

Answer: $(mass)_{KHP}$ =

b. What would be the relative standard deviation in the molarity of the base if the standard deviation in the measurement of mass in (a) is 0.0002g and this limits the precision of the calculation?

Answer: $(S_M)_{relative}$ =

11. A 50.00 ml sample of a white wine required 21.84 ml of 0.03776 M NaOH to achieve a phenophthalein end point. Express the acidity of the wine in terms of grams of tartaric acid($H_2C_4H_4O_6$; 150.09 g mol^{-1}) per 100ml.

Answer: grams $H_2C_4H_4O_6$ / 100ml =

12. What weights of Na_2HPO_4 and NaH_2PO_4 would be required to prepare 1.00L of buffer solution of pH 7.45 that has an ionic strength of 0.100:

Answer: $W_{Na_2HPO_4}$ =

$W_{NaH_2PO_4}$ =