Chemistry 142 Name \_\_\_KEY\_\_\_\_\_\_

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Exam 3 May 2009

 Page 1 (24 points)

 Page 2 (26 points)

 Page 3 (26 points)

 Page 4 (23 points)

 Page 5 (14 points)

Total (113 points)

 Percent (100 %)

**All work must be shown to receive credit. Give all answers to the correct number of significant figures**

**Constants**

|  |  |  |
| --- | --- | --- |
| NA = 6.022 x 1023 mol-1 | h=6.626x10-34 J sec | c=3.00x108 m sec-1 |
| R = 8.3145 J/(mol K) = 0.08206 L atm/(mol K) |  | F = 96,485 C/mol |

**Equations**

|  |  |  |
| --- | --- | --- |
| ΔG = ΔH – TΔS | Δ=hc/λ | ΔGo = – RT Ln Keq |
| ΔG = –nFE |  | *G* = *G*o + RT ln *Q* |
| pH= -Log[H+] | Ln [A] = Ln [A]o – kt | [A] = [A]o e- kt |
| t1/2 = Ln2/ k | 1 = 1 + 2kt [A]2 [A]o2 | Kw=Ka\*Kb |
| PT = P1 + P2 + P3 + .............. | sg = kHPg | x=-b ± (b2 – 4ac)½2a |

**The spectrochemical series:**

I- < Br- < S2- < SCN- < Cl- < NO3- < F- < OH- < C2O42- < H2O < NCS- < CH3CN < NH3 < en < bipy < phen < NO2- < PPh3 < CN- < CO



Grossmont College

Periodic Table

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  IA |  |  |  |  |  |  |  |  |  |  |  |  |  |  |  | VIIA | NOBLE GASES |
| 1**H**1.008 | IIA |  |  |  |  |  |  |  |  |  |  | IIIA | IVA | VA | VIA | 1**H**1.008 | 2**He**4.002 |
| 3**Li**6.941 | 4**Be**9.012 |  |  |  |  |  |  |  |  |  |  | 5**B**10.81 | 6**C**12.01 | 7**N**14.01 | 8**O**16.00 | 9**F**19.00 | 10**Ne**20.18 |
| 11**Na**23.00 | 12**Mg**24.30 | IIIB | IVB | VB | VIB | VIIB |  VIII VIII VIII | IB | IIB | 13**Al**27.00 | 14**Si**28.09 | 15**P**30.97 | 16**S**32.06 | 17**Cl**35.45 | 18**Ar**39.95 |
| 19**K**39.10 | 20**Ca**40.08 | 21**Sc**44.96 | 22**Ti**47.90 | 23**V**50.94 | 24**Cr**52.00 | 25**Mn**54.94 | 26**Fe**55.85 | 27**Co**58.93 | 28**Ni**58.70 | 29**Cu**63.55 | 30**Zn**65.38 | 31**Ga**69.72 | 32**Ge**72.59 | 33**As**74.92 | 34**Se**78.96 | 35**Br**79.90 | 36**Kr**83.80 |
| 37**Rb**85.47 | 38**Sr**87.62 | 39**Y**88.91 | 40**Zr**91.22 | 41**Nb**92.91 | 42**Mo**95.94 | 43**Tc**(99) | 44**Ru**101.1 | 45**Rh**102.9 | 46**Pd**106.4 | 47**Ag**107.9 | 48**Cd**112.4 | 49**In**114.8 | 50**Sn**118.7 | 51**Sb**121.8 | 52**Te**127.6 | 53**I**126.9 | 54**Xe**131.3 |
| 55**Cs**132.9 | 56**Ba**137.3 | 57**La**138.9 | 72**Hf**178.5 | 73**Ta**180.9 | 74**W**183.9 | 75**Re**186.2 | 76**Os**190.2 | 77**Ir**192.2 | 78**Pt**195.1 | 79**Au**197.0 | 80**Hg**200.6 | 81**Tl**204.4 | 82**Pb**207.2 | 83**Bi**209.0 | 84**Po**(209) | 85**At**(210) | 86**Rn**(222) |
| 87**Fr**(223) | 88**Ra**226.0 | 89**Ac**227.0 | 104**Rf**(261) | 105**Db**(262) | 106**Sg**(263) | 107**Bh**(262) | 108**Hs**(265) | 109**Mt**(266) | 110**??**(269) |  |  |  |  |  |  |  |  |

|  |  |  |  |  |  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| 58**Ce**140.1 | 59**Pr**140.9 | 60**Nd**144.2 | 61**Pm**(147) | 62**Sm**150.4 | 63**Eu**152.0 | 64**Gd**157.3 | 65**Tb**158.9 | 66**Dy**162.5 | 67**Ho**164.9 | 68**Er**167.3 | 69**Tm**168.9 | 70**Yb**173.0 | 71**Lu**175.0 |
| 90**Th**232.0 | 91**Pa**231.0 | 92**U**238.0 | 93**Np**(237) | 94**Pu**(244) | 95**Am**(243) | 96**Cm**(247) | 97**Bk**(247) | 98**Cf**(251) | 99**Es**(252) | 100**Fm**(257) | 101**Md**(258) | 102**No**(259) | 103**Lr**(260) |

Section 1: Multiple Choice (3 pts/question)

1. Molten PbCl2 is subjected to electrolysis in order to form elemental lead and chlorine. Which of the following is true?
2. Elemental chlorine gas is formed at the cathode and bubbles away
3. Elemental lead metal is formed and deposited at the anode
4. Electrons flow from the cathode to the anode
5. **Chloride ions are the reducing agents in the reaction**
6. none of the above

Pb2+(aq) + 2e- 🡪 Pb(s) -0.13 V Reduction, oxidizing agent, cathode

2Cl-(aq) 🡪 Cl2(g) + 2e- - 1.36 V Oxidation, reducing agent, anode

1. A metal can be protected from corrosion by making it:
2. Either electrode in an electrochemical cell.
3. The electrolyte in an electrochemical cell.
4. **The cathode in an electrochemical cell.**
5. The anode in an electrochemical cell.
6. none of the above
7. Use Eo value to calculate Ksp of Ni(OH)2 at 25oC (hint one of the electrodes is Ni (s))
8. **2 x10-16** b) 6x1010 c) 30 d) 1 x10-9 e) 4x10-13

Ni(OH)2 (s) + 2e- 🡪 Ni(s) + 2OH-(aq) -0.72 V

Ni(s) 🡪 Ni2+(aq) + 2e- 0.23 V

Ni(OH)2 🡪 Ni2+(aq) + 2OH-(aq) -0.49 V

ΔG = –nFEmole- \* 96,485 C/mol\*(-0.49 V) = 9.46 x104 J

Ln Ksp = – ΔGo /RT = 9.46 x104 J / (8.3145 J/(mol K) \*298 K) = -38.18

Ksp = 2.6x10-17

1. Rank Sn2+ (aq), I- (aq) and Cu (s) in order of strongest to weakest reducing agent
2. I- (aq) > Sn2+ (aq) > Cu (s) **b) Sn2+ (aq) > Cu (s) > I- (aq)** c) Cu (s) > I- (aq) > Sn2+ (aq)
3. I- (aq) > Cu (s) > Sn2+ (aq) e) Cu (s) > Sn2+ (aq) > I- (aq)

Sn2+(aq) 🡪 Sn4+(aq) + 2e --0.15 V

Cu(s) 🡪 Cu2+ (aq) + 2e- -0.34 V

2I-(aq) 🡪 I2(s) + 2e- -0.54 V

1. The tetrahedral complex ion [Cu(H2O)4]2+ has magnetic properties that correspond to how many unpaired electrons?

a) 4 b) 3 c) 2 **d) 1** e) 0



Cu2+ [Ar]3d9

1. A bidentate ligand always
2. Has bonds formed to two metal ions
3. **Has two donar atoms**
4. Has a charge of 2+ or 2-.
5. Forms complex ions with a charge of 2+ or 2-.
6. Has medical uses.
7. A particular complex ion is observed to have an orange red color at approximate wavelength of 630 nm. What is the value of the crystal field splitting energy for this complex

a) 188.5 kJ/mol b) 171 kJ/mol c) 213.8 kJ/mol

d) 278.4 kJ/mol **e) 249.3 kJ/mol**

Wavelength absorbed 480 nm ∆E = 6.626 x 10-34 J\*s (3.00 x 108 m/s) = 4.14 x 10-19 J/particle

480 x 10-9 m

4.14 x 10-19 J/particle \* 1kJ/1000 J \* (6.022 x 1023 particles / 1mol) = 249 kJ/mol

1. In the qualitative analysis schemes, initial separation of the metal cations into various groups is based on\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_
2. Difference in acid/base properties of the metal cations
3. Amphoteric properties
4. **Difference in Ksp values**
5. Ability to form ammonia complexes
6. Hydrolysis of the metal cation

Section 2: Short answer/ essay

1. Consider a voltaic cell based on the following unbalanced reaction

Pb (s) + IO3- (aq) 🡪 Pb2+ (aq) + I2(s)

1. Write the balanced oxidation and reduction half reactions under acidic conditions (label which is oxidation and which is reduction), the overall reaction equation and calculate Eocell. (9 pts)

Oxidation: \_\_\_\_\_\_\_\_\_5\*(Pb (s) 🡪 Pb2+ (s) + 2 e-)\_\_\_\_\_\_\_\_\_\_\_\_\_

Reduction: \_\_\_\_\_\_\_\_10 e- 12 H+ +2 IO3- (aq) 🡪 I2(s) + 6 H2O \_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_\_

Overall Reaction: \_\_\_\_\_ 5 Pb (s) + 2 IO3- (aq) +12 H+ 🡪 5 Pb2+ (aq) + I2(s) + 6 H2O \_\_\_\_\_\_\_\_\_\_\_\_

1. Write the line notation for the cell \_\_Pb(s)/Pb2+║ IO3-,H+/ I2(s),Pt(s)\_\_\_ (3 pts)
2. Draw a fully labeled Free energy diagram for this reaction at 298 K. Indicate and clearly label on the diagram (i) a point where the reaction is spontaneous, and (ii) the equilibrium point. Explain your logic behind your graph (calculations are not necessary). (6 pts)

ΔGo

 Reactant

Explain: EΔG = -

Free

Energy

Spont Rxn

ΔGo

 Products

Equil

Products

Reactants

1. Draw a picture of the cell. Indicate the composition of all parts of the cell, the direction of electron flow, and the direction of ion movements within each compartment. (8 pt)



1. Give the IUPAC name or formula, oxidation state, coordination number and electron configuration (8 pts)

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Name** | **Formula** | **Oxidation #** | **Coordination #** | **Electron Config** |
| amminecyanobis(ethylenediammine)colbalt(III) ion | [Co(en)2(NH3)(CN)] 2+ | +3 | 6 | [Ar] 3d6 |
| potassium trichlorosulfatoplatinate(II) | K3[PtCl3(SO4)] | +2 | 4 | [Xe] 4f145d8 |

1. How does Crystal Field theory account for the following observations? In each part, ***show* and *explain***the relative positions of the orbital’s and the number of electrons in each.(18 pts)
	1. [Ru(H2O)6]2+ is found to be paramagnetic whereas [Ru(CN)6]4─ is found to be diamagnetic.

The Ru2+ is a d6 metal ion. Given the ligand identity in each, the [Ru(H2O)6]2+ complex will most likely have a smaller Δ than the [Ru(CN)6]4─ complex since H2O is a weaker ligand than CN.



When electrons are distributed in this scenario, we see that the CN complex pairs up the electrons in the lower orbitals given all paired (diamagnetic). The H2O complex has electrons placed into the all the orbital before pairing, thereby giving 4 unpaired electrons total (paramagnetic).

* 1. The color of a solution of [V(CN)6]4─ ions appears yellow whereas a solution of [V(H2O)6]2+ appears blue.

The metal is V2+ in both complexes. This is d3. CN- is a stronger ligand than H2O and therefore Δ for [Cr(CN)6]4─ is larger than that for [Cr(H2O)6]2+. We also know that the CN complex looks yellow which means it absorbs violet light and the H2O complex looks blue so it absorbs orange light.



Since the CN complex has a larger Δ, it will absorb a higher energy light (violet in this case).

The H2O complex has a lower Δ and will absorb a lower energy light (orange in this case).

* 1. A solution of [Cd(H2O)6]2+ is colorless.

The metal is Cd2+ in this complex with gives it a d10 configuration. Ten electrons will fill all of the orbitals and pair in this complex. In order for a molecule to have ‘color’ there needs to be an excitation of an electron from the lower to the upper orbital when it absorbs light. Unfortunately, in this case, the electrons have no place to go since we’ve filled all of the d orbitals. Therefore, no light will be absorbed and no electrons will ‘jump’.

1. A Zn/Cu ***battery*** is constructed based on the following electrochemical cell in which the volume of solution in each half-cell is 250 mL.

Zn(s) **|** Zn2+ (0.100 M) **||** Cu2+ (1.50 M) **|** Cu(s)

1. This battery is pronounced "dead" when 99 % of its chemical capacity is used up (i.e., when the concentration of Cu2+ has dropped to 1.00 % of its initial value). Calculate the cell potential (in volts) of the battery at this point. (8 pts)

*E*ocell = *E*ocathode - *E*oanode = 0.34 v – (-0.76 v) = 1.10 v

Final [Cu2+] = 1.00 % of 1.50 M = 0.015 M

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
|  | Zn(s) | **+** Cu2+ | 🡪Cu(s) | + Zn2+ |
| I | ---- | 1.50 M | ------ | 0.100 M |
| C |  | -x |  | +x |
| E |  | 0.015 |  | 1.585 M |

1.50-x= 0.015 🡪 -x =0.015 -1.50 🡪 x =1.485

 Zn2+ =1.00 M + x =0.100 M + 1.485 = 1.585 M

*E* = *E*o -(0.0592/n) log K where K= [Zn2+] / [Cu2+]

= 1.10 - (0.0592/2) log(1.585 / 0.015)

= 1.10 - 0.060 = 1.04 v

1. Determine the length of time (in hours) that this battery could supply a current of 1.50 amps until it dies (based on the same 99 % definition of "dead"). (6 pts)

moles of Cu2+ consumed = 0.3713 moles

(0.3713 mole Cu2+) (2 mole e- / mole Cu2+) (96,500 coul / mole e-)

= 71651 coul = 71651 amp.sec

time = (71651 amp.sec) (1 hr / 3600 sec) / 1.50 amp = 13.3 hr

1. The following cations Hg22+, Pb2+ and Ag+ are present in solution. List the ions or compounds that would be found from the following observations. (9 pts)
	1. Forms a chloride precipitate that is soluble in or reacts with NaOH solution

Hg2Cl2, PbCl2and AgCl + NaOH 🡪 **[Pb(OH)4]2–**

* 1. Forms a chloride precipitate that is soluble in aqueous ammonia (NH3) solution

Hg2Cl2, PbCl2and AgCl + NH3 🡪 **[Ag(NH3)2]+**

* 1. Forms a white chloride precipitate, when treated with excess aqueous ammonia (NH3) solution a black precipitate forms

Hg2Cl2, PbCl2and AgCl + NH3 (excess) 🡪 **Hg (s) + HgNH2Cl**

1. Define the following
	1. *geometric isomerism* and *optical isomerism (4pts)*

*Geometric isomerism:* are isomers which the atoms are joined to one another in the same way but but occupy different relative position

*Optical isomerism:* are isomers that are non-super imposable mirror images

* 1. Give an example of each using [Pd(C2O4)2Br2]2+. Make sure to give specific labels to each according to the type of isomerism. (6pts)

 

1. Explain why potassium metal cannot be electroplated from an aqueous solution. (4pts)

K+(aq) + e- -> K(s) (-2.92 V) competes with 2H2O(l) + 2e- -> H2(g) + 2OH-(aq) (-0.83 V)

If the reduction of water is easier as in this case than the reduction of the potassium ion to the potassium solid, then water will be reduced instead of the potassium ion

Only metal ions with E° red more positive than -0.83 V can be electroplated as metal solid in water

1. Apply the valence bond theory to predict and diagram the type of hybrid orbital utilized for bonding by the metal ions in each of the following:
2. [Fe(H2O)6] 2+ , diamagnetic [Ar] 3d6



1. [CoCl4]2-, paramagnetic with three unpaired electrons [Ar] 3d7



**Standard Electrode Potentials in Aqueous Solution at 25°C**

|  |  |  |  |
| --- | --- | --- | --- |
| Cathode (Reduction)Half-Reaction | E° (volts) | Cathode (Reduction)Half-Reaction | E° (volts) |
| Li+(aq) + e- -> Li(s) | -3.04 | Cu+(aq) + e- -> Cu(s) | 0.52 |
| K+(aq) + e- -> K(s) | -2.92 | I2(s) + 2e- -> 2I-(aq) | 0.54 |
| Ca2+(aq) + 2e- -> Ca(s) | -2.76 | ClO2-(aq) + H2O(l) + 2e- -> ClO-(aq) + 2OH-(aq) | 0.59 |
| Mg2+(aq) + 2e- -> Mg(s) | -2.38 | Fe3+(aq) + e- -> Fe2+(aq) | 0.77 |
| Al3+(aq) + 3e- -> Al(s) | -1.66 | Hg22+(aq) + 2e- -> 2Hg(l) | 0.80 |
| 2H2O(l) + 2e- -> H2(g) + 2OH-(aq) | -0.83 | Ag+(aq) + e- -> Ag(s) | 0.80 |
| Zn2+(aq) + 2e- -> Zn(s) | -0.76 | Hg2+(aq) + 2e- -> Hg(l) | 0.85 |
| Cr3+(aq) + 3e- -> Cr(s) | -0.74 | ClO-(aq) + H2O(l) + 2e- -> Cl-(aq) + 2OH-(aq) | 0.90 |
| Ni(OH)2 (s) + 2e- -> Ni(s) + 2OH-(aq) | -0.72 | 2Hg2+(aq) + 2e- -> Hg22+(aq) | 0.90 |
| Fe2+(aq) + 2e- -> Fe(s) | -0.41 | NO3-(aq) + 4H+(aq) + 3e- -> NO(g) + 2H2O(l) | 0.96 |
| Cd2+(aq) + 2e- -> Cd(s) | -0.40 | Br2(l) + 2e- -> 2Br-(aq) | 1.07 |
| Ni2+(aq) + 2e- -> Ni(s) | -0.23 | IO3-(aq) + 6H+(aq) + 5e- -> ½ I2(s) + 3H2O(l) | 1.20 |
| Sn2+(aq) + 2e- -> Sn(s) | -0.14 | O2(g) + 4H+(aq) + 4e- -> 2H2O(l) | 1.23 |
| Pb2+(aq) + 2e- -> Pb(s) | -0.13 | Cr2O72-(aq) + 14H+(aq) + 6e- -> 2Cr3+(aq) + 7H2O(l) | 1.33 |
| Fe3+(aq) + 3e- -> Fe(s) | -0.04 | Cl2(g) + 2e- -> 2Cl-(aq) | 1.36 |
| 2H+(aq) + 2e- -> H2(g) | 0.00 | Ce4+(aq) + e- -> Ce3+(aq) | 1.44 |
| Sn4+(aq) + 2e- -> Sn2+(aq) | 0.15 | MnO4-(aq) + 8H+(aq) + 5e- -> Mn2+(aq) + 4H2O(l) | 1.49 |
| Cu2+(aq) + e- -> Cu+(aq) | 0.16 | H2O2(aq) + 2H+(aq) + 2e- -> 2H2O(l) | 1.78 |
| AgCl(s) + e- -> Ag(s) + Cl-(aq) | 0.22 | Co3+(aq) + e- -> Co2+(aq) | 1.82 |
| Cu2+(aq) + 2e- -> Cu(s) | 0.34 | S2O82-(aq) + 2e- -> 2SO42-(aq) | 2.01 |
| ClO3-(aq) + H2O(l) + 2e- -> ClO2-(aq) + 2OH-(aq) | 0.35 | O3(g) + 2H+(aq) + 2e- -> O2(g) + H2O(l) | 2.07 |
| IO-(aq) + H2O(l) + 2e- -> I-(aq) + 2OH-(aq) | 0.49 | F2(g) + 2e- -> 2F-(aq) | 2.87 |

**Solubility Constants at 25****C**

|  |  |  |  |
| --- | --- | --- | --- |
| Name | Ksp | Name | Ksp |
| Silver chloride | 1.77×10-10 | Manganese (II) hydroxide | 1.6 x 10-13 |
| Barium fluoride | 1.7 x 10-6 | Lead (II) hydroxide | 2.8 x 10-16 |
| Barium phosphate | 6 x 10-39 | Lead (II) phosphate | 3.0 x 10-44 |
| Barium sulfate | 1.1 x 10-10 | Lead (II) Sulfide | 3.2 x 10-28 |
| Cadmium carbonate | 1.0×10-12 | Lead (II) Sulfate | 1.8 x 10-8 |
| Cadmium hydroxide | 7.2×10-15 | Nickel(II) carbonate | 6.6 x 10-9 |
| Cadmium phosphate | 2.53×10-33 | Nickel(II) hydroxide | 2.8 x 10-16 |
| Cadmium sulfide | 1×10-27 | Nickel(II) phosphate | 4.74×10-32 |
| Iron (II) carbonate | 2.1 x 10-11 | Nickel(II) sulfide | 4×10-20 |
| Iron (II) hydroxide | 7.9 x 10-16 | Tin(II) hydroxide | 5.45×10-27 |
| Mercury(I) carbonate | 3.6×10-17 | Tin(II) sulfide | 1×10–70 |
| Mercury(I) chloride | 1.43×10-18 |  |  |

## Formation Constants for Complex Ions at 25 oC.

|  |  |  |  |
| --- | --- | --- | --- |
| Complex Ion | Kf | Complex Ion | Kf |
| [Ag(NH3)2]+ | 1.6×107 | [PbI4]2– | 3.0×104 |
| [Cd(en)3]2+ | 1.2×1012 | [Pb(OH)4]2– | 3.8×1014 |
| [Cd(NH3)4]2+ | 1.3×107 | [Pb(ox)2]2– | 3.5×106 |
| [Ni(CN)4]2– | 2×1031 | [HgCl4]2 |  5.0 x 1015 |
| [Ni(EDTA)]2– | 3.6×1018 | [Hg(NH3)4]2+  | 1.8 x 1019 |
| [Ni(en)3]2+ | 2.1×1018 | [SnF6]2- | 1.0 x 1025 |
| [Ni(NH3)6]2+ | 5.5×108 | SnS32- | 2.1×1018 |
| [PbCl3]– | 2.4×101 | SnCl62- | 6.8×1029 |
| [Pb(EDTA)]2– | 2×1018 |  |  |