Chemistry 10123, **Exam 4** **Answer Key**
April 10, 2019

1. (10 points) Use the ion-electron method to balance the following redox reaction that occurs in ***basic*** solution. Write ***complete, balanced equations*** for the individual half-reactions and for the overall net ionic equation. Also, ***circle the reducing agent*** in this reaction.

$$N_3^-(aq) + S_2O_3^{2-}(aq) \longrightarrow SO_3^{2-}(aq) + NH_3(aq)$$

(reducing agent)

Reduction Half Reaction:

$$8\,e^- + 9\,H_2O + N_3^- \longrightarrow 3\,NH_3 + 9\,OH^-$$

Oxidation Half Reaction:

$$6\,OH^- + S_2O_3^{2-} \longrightarrow 2\,SO_3^{2-} + 3\,H_2O + 4\,e^- \qquad (\times 2)$$

Net Ionic Equation:

$$3\,H_2O + 3\,OH^- + N_3^- + 2\,S_2O_3^{2-} \longrightarrow 3\,NH_3 + 4\,SO_3^{2-}$$

2. (3 points) A compound sometimes called "calcium cerium selenate" has the formula $CaCe(SeO_4)_3$. Give the oxidation states of all four elements in this compound.

Ca = + 2 O = - 2 Ce = + 4 Se = + 6

3. (10 points) **SHOW ALL WORK.** A 100.0 mL sample of a solution of Sn^{2+} required 42.15 mL of 0.1100 M $KMnO_4$ to reach the equivalence point in a titration. Assuming that the main products of the redox reaction are Sn^{4+} and Mn^{2+}, determine the molarity of the Sn^{2+} solution. (***Note***: Your answer must include the ***balanced, net-ionic equation*** for the titration reaction, in acidic solution.)

oxid: $Sn^{2+} \longrightarrow Sn^{4+} + 2\,e^-$ (x 5)

red: $5\,e^- + 8\,H^+ + MnO_4^- \longrightarrow Mn^{2+} + 4\,H_2O$ (x 2)

net Rx: $5\,Sn^{2+} + 16\,H^+ + 2\,MnO_4^- \longrightarrow 2\,Mn^{2+} + 8\,H_2O + 5\,Sn^{4+}$

(0.04215 L) (0.110 mole MnO_4^- / L) (5 mole Sn^{2+} / 2 mole MnO_4^-)

= 0.01159 mole Sn^{2+}

(0.01159 mole Sn^{2+}) / (0.100 L) = 0.116 M Sn^{2+}

4. (6 points) Write ***balanced ionic equations*** for the half-reactions.

(a) The ***cathode*** reaction in the electrolysis of *aqueous* KNO_3.

$$2\,H_2O \;+\; 2\,e^- \longrightarrow H_2 \;+\; 2\,OH^-$$

(b) The ***anode*** reaction in the electrolysis of *molten* Al_2O_3.

$$2\,O^{2-} \longrightarrow O_2 \;+\; 4\,e^-$$

(c) The ***anode*** reaction in the electrolysis of *aqueous* Na_2SO_4.

$$2\,H_2O \longrightarrow O_2 \;+\; 4\,H^+ \;+\; 4\,e^-$$

5. Consider the following reaction and the related thermodynamic data below.

$$3\,SO_{2(g)} \;+\; 2\,NO_{2(g)} \longrightarrow 3\,SO_{3(g)} \;+\; N_2O_{(g)}$$

Compound	Standard Heat of Formation ($\Delta H°_f$) in kJ/mole	Standard Entropy ($S°$) in J/mole·K
$NO_{2(g)}$	33	240
$N_2O_{(g)}$	82	221
$SO_{2(g)}$	- 297	248
$SO_{3(g)}$	- 396	257

(a) (10 points) **SHOW ALL WORK.** Is the above reaction spontaneous at 25 °C? Determine the appropriate thermodynamic quantity that is required in order to answer this question.

$\Delta H° = 3(-396) + 82 - [\,3(-297) + 2(33)\,] = -281$ kJ

$\Delta S° = 3(257) + 221 - [\,3(248) + 2(240)\,] = -232$ J/K $= -0.232$ kJ/K

$\Delta G° = \Delta H° - T\Delta S° = -281$ kJ $- (298$ K$)(-0.232$ kJ/K$) = -212$ kJ

Negative $\Delta G°$ indicates that the reaction is spontaneous at 25 °C.

(b) (10 points) **SHOW ALL WORK.** Determine the ***equilibrium constant*** (K_p) for the above reaction at 600 °C. (600 + 273 = 873 K)

Since $\Delta H°$ and $\Delta S°$ are relatively independent of temp, their values at 298 K can be used to estimate $\Delta G°$ (and K) at another temp. At 873 K:

$\Delta G = (-281$ kJ$) - (873$ K$)(-0.232$ kJ/K$) = -78.5$ kJ

$\Delta G = -RT\ln K$

$\ln K = -\Delta G / RT = -(-78.5$ kJ / mole$) / (8.314 \times 10^{-3}$ kJ/mole·K$)(873$ K$)$

$\ln K = 10.81$

$K = 4.95 \times 10^4$

6. A Zn/Ag ***battery*** is constructed based on the following electrochemical cell in which the volume of solution in each half-cell is 0.500 L.

$$Zn_{(s)} \mid Zn^{2+}\ (0.100\ M) \parallel Ag^{+}\ (1.500\ M) \mid Ag_{(s)}$$

(a) (6 points) Write ***balanced chemical equations*** for the half-reactions and the overall ***cell reaction*** occurring in this device. Also, determine the ***standard cell potential*** (E^{o}_{cell}).

cathode reaction:

$Ag^{+}_{(aq)} + e^{-} \longrightarrow Ag_{(s)}$ $\qquad E^{\circ}_{red} = +\ 0.80\ v$

anode reaction:

$Zn_{(s)} \longrightarrow Zn^{2+}_{(aq)} + 2\ e^{-}$ $\qquad E^{\circ}_{oxid} = -\ (-\ 0.76\ v) = +\ 0.76\ v$

cell reaction:

$Zn_{(s)} + 2\ Ag^{+}_{(aq)} \longrightarrow Zn^{2+}_{(aq)} + 2\ Ag_{(s)}$

$E^{\circ}_{cell} = 0.80 + 0.76 = 1.56\ v$

(b) (10 points) **SHOW ALL WORK.** This battery is pronounced "dead" when 98 % of its chemical capacity is used up (i.e., when the concentration of the major reactant has dropped to 2.00 % of its initial value). Calculate the cell potential (in volts) of the battery at this point.

Initially, moles Ag^{+} = (0.500 L) (1.50 mole/L) = 0.750 moles

moles Zn^{2+} = (0.500 L) (0.100 mole/L) = 0.0500 moles

moles Ag^{+} remaining = 2.00 % of 0.750 = (0.020) (0.750) = 0.015 moles

$[Ag^{+}]$ = 0.015 mole / 0.500 L = 0.0300 M

moles Ag^{+} consumed = 0.750 moles - 0.015 moles = 0.735 moles

moles Zn^{2+} formed = (0.735 mole Ag^{+}) (1 mole Zn^{2+} / 2 mole Ag^{+})

= 0.3675 moles

moles Zn^{2+} remaining = 0.0500 + 0.3675 = 0.4175 moles

$[Zn^{2+}]$ = 0.4175 mole / 0.500 L = 0.835 M

$Q = [Zn^{2+}] / Ag^{+}]^{2} = 0.835 / (0.0300)^{2} = 927.8$

$E_{cell} = E^{\circ}_{cell} - (0.0592/n) \log Q = 1.56 - (0.0592 / 2) \log(927.8)$

$E_{cell} = 1.56 - 0.088 = 1.47\ v$

(c) (8 points) **SHOW ALL WORK.** Determine the current (in amps) that this battery could produce if it is operated continuously for 24 hours until it dies (based on the same 98 % definition of "dead"). (***Note***: The cell potentials from parts a and/or b above are not required here!)

moles Ag^{+} consumed = 0.735 moles

(0.735 mole Ag^{+}) (1 mole e^{-} / 1 mole Ag^{+}) = 0.735 mole e^{-}

(0.735 mole e^{-}) (96,500 coul / mole e^{-}) (1 amp·sec / coul) = 7.093×10^{4} amp·sec

(7.093×10^{4} amp·sec) / (24 hr) (3600 sec/hr) = 0.82 amps

7. (8 points) **SHOW ALL WORK.** A solution containing tungsten (W) ion in an unknown oxidation state was electrolyzed with a current of 1.25 amp for 6.00 hours. During this process, 12.86 g of metallic tungsten was deposited at the cathode. Determine the oxidation state of the tungsten ion in the original solution.

$W^{n+} + n\,e^- \longrightarrow W$ $\qquad$ $n = \text{moles } e^- / \text{moles W}$

(1.25 amp) (6 hr) (3600 sec/hr) = 27,000 amp·sec = 27,000 coul

(27,000 coul) (1 mole e^- / 96,500 coul) = 0.280 mole e^-

(12.86 g W) (1 mole W / 183.85 g) = 0.0700 mole W

n = 0.280 / 0.0700 = 4 $\qquad$ ∴ oxidation state is W^{4+}

8. (4 points) Arrange the following substances in order of increasing standard molar entropy (S°).

$CO_{2(g)}$ $\quad$ $Ar_{(g)}$ $\quad$ $N_{2(g)}$ $\quad$ $CH_3NH_{2(g)}$ $\quad$ $Ne_{(g)}$ $\quad$ $NH_{3(g)}$

$Ne < Ar < N_2 < NH_3 \approx CO_2 < CH_3NH_2$

lowest S° $\qquad$ highest S°

9. (8 points) **SHOW ALL WORK.** Use appropriate electrochemical data to determine the ***formation constant*** **(K_f)** for $PtCl_4^{2-}{}_{(aq)}$. ***Include balanced chemical equations for all relevant reactions***.

$Pt^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Pt_{(s)}$ $\qquad$ $E°_{red} = 1.18$ v

$Pt_{(s)} + 4\,Cl^-{}_{(aq)} \longrightarrow PtCl_4^{2-}{}_{(aq)} + 2\,e^-$ $\qquad$ $E°_{oxid} = -(0.76$ v$)$

$Pt^{2+}{}_{(aq)} + 4\,Cl^-{}_{(aq)} \rightleftharpoons PtCl_4^{2-}{}_{(aq)}$

$E°_{cell} = 1.18 - 0.76 = 0.42$ v

$\log K_f = n\,E°_{cell} / 0.0592 = 2\,(0.42) / 0.0592 = 14.19$

$K_f = 1.55 \times 10^{14}$

10. (7 points) **SHOW ALL WORK.** Acetone (a common organic liquid) has a normal boiling point of 56.1 °C, a heat of vaporization of 31.3 kJ/mole, and a standard molar entropy [$S°_{(liq)}$] of 200.4 J/mole·K. Calculate the standard molar entropy [$S°_{(g)}$] of gaseous acetone (in J/mole·K).

$\Delta G = \Delta H - T\Delta S = 0$ $\qquad$ (at equilibrium)

$\Delta S = \Delta H / T = 31{,}300 \text{ J} / (56.1 + 273.15) \text{ K} = 95.1$ J/K

$\Delta S = 95.1 \text{ J/K} = S°_{(g)} - S°_{(liq)} = S°_{(g)} - 200.4$ J/mole·K

$S°_{(g)} = 296$ J/mole·K

Standard Reduction Potentials

Half - Reaction	***E*° (volts)**
$Au^{3+}{}_{(aq)} + 3\,e^- \longrightarrow Au_{(s)}$	+ 1.50
$Cl_{2(g)} + 2\,e^- \longrightarrow 2\,Cl^-{}_{(aq)}$	+ 1.36
$O_{2(g)} + 4\,H^+{}_{(aq)} + 4\,e^- \longrightarrow 2\,H_2O$	+ 1.23
$Pt^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Pt_{(s)}$	+ 1.18
$AuCl_4{}^-{}_{(aq)} + 3\,e^- \longrightarrow Au_{(s)} + 4\,Cl^-{}_{(aq)}$	+ 1.00
$Ag^+{}_{(aq)} + e^- \longrightarrow Ag_{(s)}$	+ 0.80
$Fe^{3+}{}_{(aq)} + e^- \longrightarrow Fe^{2+}{}_{(aq)}$	+ 0.77
$PtCl_4{}^{2-}{}_{(aq)} + 2\,e^- \longrightarrow Pt_{(s)} + 4\,Cl^-{}_{(aq)}$	+ 0.76
$Cu^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Cu_{(s)}$	+ 0.34
$AgCl_{(s)} + e^- \longrightarrow Ag_{(s)} + Cl^-{}_{(aq)}$	+ 0.22
$Cu^{2+}{}_{(aq)} + e^- \longrightarrow Cu^+{}_{(aq)}$	+ 0.16
$2\,H^+{}_{(aq)} + 2\,e^- \longrightarrow H_{2(g)}$	0.00
$Pb^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Pb_{(s)}$	- 0.13
$Ni^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Ni_{(s)}$	- 0.23
$PbSO_{4(s)} + 2\,e^- \longrightarrow Pb_{(s)} + SO_4{}^{2-}{}_{(aq)}$	- 0.36
$Fe^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Fe_{(s)}$	- 0.44
$PbO_{(s)} + H_2O + 2\,e^- \longrightarrow Pb_{(s)} + 2\,OH^-{}_{(aq)}$	- 0.58
$Zn^{2+}{}_{(aq)} + 2\,e^- \longrightarrow Zn_{(s)}$	- 0.76
$2\,H_2O + 2\,e^- \longrightarrow H_{2(g)} + 2\,OH^-{}_{(aq)}$	- 0.83
$Al^{3+}{}_{(aq)} + 3\,e^- \longrightarrow Al_{(s)}$	- 1.66
$Na^+{}_{(aq)} + e^- \longrightarrow Na_{(s)}$	- 2.21
$K^+{}_{(aq)} + e^- \longrightarrow K_{(s)}$	- 2.92

Periodic Table of the Elements

	IA (1)	IIA (2)	IIIB (3)	IVB (4)	VB (5)	VIB (6)	VIIB (7)	........VIIIB........ (8)	(9)	(10)	IB (11)	IIB (12)	IIIA (13)	IVA (14)	VA (15)	VIA (16)	VIIA (17)	VIIIA (18)
1	1 **H** 1.0080																	2 **He** 4.0026
2	3 **Li** 6.9410	4 **Be** 9.0122											5 **B** 10.811	6 **C** 12.011	7 **N** 14.007	8 **O** 15.999	9 **F** 18.998	10 **Ne** 20.179
3	11 **Na** 22.990	12 **Mg** 24.305											13 **Al** 26.982	14 **Si** 28.086	15 **P** 30.974	16 **S** 32.066	17 **Cl** 35.453	18 **Ar** 39.948
4	19 **K** 39.098	20 **Ca** 40.078	21 **Sc** 44.956	22 **Ti** 47.880	23 **V** 50.942	24 **Cr** 51.996	25 **Mn** 54.938	26 **Fe** 55.847	27 **Co** 58.933	28 **Ni** 58.690	29 **Cu** 63.546	30 **Zn** 65.380	31 **Ga** 69.723	32 **Ge** 72.610	33 **As** 74.922	34 **Se** 78.960	35 **Br** 79.904	36 **Kr** 83.800
5	37 **Rb** 85.468	38 **Sr** 87.620	39 **Y** 88.906	40 **Zr** 91.224	41 **Nb** 92.906	42 **Mo** 95.940	43 **Tc** 98.907	44 **Ru** 101.07	45 **Rh** 102.91	46 **Pd** 106.42	47 **Ag** 107.87	48 **Cd** 112.41	49 **In** 114.82	50 **Sn** 118.71	51 **Sb** 121.75	52 **Te** 127.60	53 **I** 126.90	54 **Xe** 131.29
6	55 **Cs** 132.91	56 **Ba** 137.33	57 **La** 138.91	72 **Hf** 178.49	73 **Ta** 180.95	74 **W** 183.85	75 **Re** 186.21	76 **Os** 190.20	77 **Ir** 192.22	78 **Pt** 195.09	79 **Au** 196.97	80 **Hg** 200.59	81 **Tl** 204.38	82 **Pb** 207.20	83 **Bi** 208.98	84 **Po** 208.98	85 **At** 209.99	86 **Rn** 222.02
7	87 **Fr** 223.02	88 **Ra** 226.03	89 **Ac** 227.03	104 Unq 261.11	105 Unp 262.11	106 Unh 263.12	107 Uns 262.12											