Chemistry 210

Exam 4

Be sure to put your name on each page. This page can be removed from your exam so that you will have a Periodic Table handy throughout the exam, it does not need to be turned in. Show all your work for problems which require any sort of calculation, no credit will be given for answers without work shown. If you have shown a significant amount of work or multiple drawings for a problem, draw a box around what you consider your final answer.

Avogadro's Number = 6.022×10^{23} ^{units}/_{mol} 32.00°F = 0.000°C = 273.15KDensity of Water = $1.000^{g}/_{mL}$ R = $0.08206^{L*atm}/_{mol*K} = 8.314^{J}/_{mol*K}$ 1atm = 760torr = 760mmHg = 101.325kPaPV=nRT $\Delta T_{fp/bp} = k_{fp/bp} \cdot m \cdot i$ For water: $k_{fp} = -1.86^{\circ C}/_{m}$ $k_{bp} = 0.512^{\circ C}/_{m}$ P₁ = $X_1P_1^{\circ}$ $\Pi = MRTi$ $C_1V_1 = C_2V_2$ Quadratic formula: $\chi = -b \pm \sqrt{b^2 - 4ac}$

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

Integrated Rate Laws: $\begin{array}{ll} 0^{th} & [A]_{t} = -kt + [A]_{o} \\ 1^{st} & \ln[A]_{t} = -kt + \ln[A]_{o} \\ 2^{nd} & 1/[A]_{t} = kt + 1/[A]_{o} \\ k = Ae^{-Ea/RT} \end{array}$ $\ln(k) = \left(\frac{-E_{a}}{R}\right) \left(\frac{1}{T}\right) + \ln(A)$ $\ln\left(\frac{k_{1}}{k_{2}}\right) = \frac{E_{a}}{R} \left(\frac{1}{T_{2}} - \frac{1}{T_{1}}\right)$ $pH = pK_{a} + \log\left(\frac{[\text{conjugate base}]}{[\text{conjugate acid}]}\right)$

If you use $C_1V_1 = C_2V_2$ to calculate a titration, you will receive zero points for that problem.

$$\begin{split} E_{cell} &= E_{cell}^{o} - {}^{RT}/{}_{nF} lnQ \\ E_{cell}^{o} &= {}^{RT}/{}_{nF} lnK^{o} \\ K^{o} &= e^{A} ({}^{nF}/{}_{RT} E_{cell}^{o}) \\ F &= 96485 {}^{J}/{}_{V \text{-mol of electrons}} \\ \Delta G^{o} &= \Delta H^{o}_{system} - T\Delta S_{system}^{o} \\ \Delta G^{o} &= -nFE_{cell}^{o} &= -RT lnK^{o} \\ \Delta G &= \Delta G^{o} + RT lnQ \\ F &= 96485 {}^{C}/{}_{mol electrons} \\ 1A &= 1 C / sec \end{split}$$

1																	2
Η																	He
1.0079		_															4.0026
3	4											5	6	7	8	9	10
Li	Be											B	С	Ν	Ο	\mathbf{F}	Ne
6.941	9.0122											10.811	12.011	14.007	15.999	18.998	20.180
11	12											13	14	15	16	17	18
Na	Mg											Al	Si	Ρ	S	Cl	Ar
22.990	24.305											26.982	28.086	30.974	32.066	35.453	39.948
19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
Κ	Ca	Sc	Ti	V	Cr	Mn	Fe	Со	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
39.098	40.078	44.956	47.88	50.942	51.996	54.938	55.847	58.933	58.69	63.546	65.39	69.723	72.61	74.922	78.96	79.904	83.80
37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	Ι	Xe
85.468	87.62	88.906	91.224	92.906	95.94	(98)	101.07	102.91	106.42	107.87	112.41	114.82	118.71	121.76	127.60	126.90	131.29
55	56	71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
Cs	Ba	Lu	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
132.91	137.33	174.97	178.49	180.95	183.84	186.21	190.23	192.22	195.08	196.97	200.59	204.38	207.2	208.98	(209)	(210)	(222)
87	88	103	104	105	106	107	108	109	110	111	112	113	114	115	116	117	118
Fr	Ra	Lr	Rf	Db	Sg	Bh	Hs	Mt	Ds	Rg	Cn		Fl		Lv		
(223)	226.03	(260)	(261)	(262)	(263)	(262)	(265)	(266)	(269)	(272)	(277)						

57	58	59	60	61	62	63	64	65	66	67	68	69	70
La	Ce	Pr	Nd	Pm	Sm	Eu	Gd	Tb	Dy	Ho	Er	Tm	Yb
138.91	140.12	140.91	144.24	(145)	150.36	151.97	157.25	158.93	162.50	164.93	167.26	168.94	173.04
89	90	91	92	93	94	95	96	97	98	99	100	101	102
Ac	Th	Pa	U	Np	Pu	Am	Cm	Bk	Cf	Es	Fm	Md	No
227.03	232.04	231.04	238.03	237.05	(244)	(243)	(247)	(247)	(251)	(252)	(258)	(258)	(259)

Multiple Choice (5pts each): Circle the letter of the most correct response.

- 1. According to the Lewis definitions of acids and bases:
 - a. A base is a source of hydroxide ions
 - b. A base accepts electrons
 - c. An acid donates H^+
 - d. An acid accepts electron pairs
 - e. A base accepts H⁺

2. A reaction will be product-favored/spontaneous if:

- a. $\Delta G^{\circ} < 0$
- b. $K_{eq} < 1$
- c. $\Delta \dot{H} > 0$
- d. $\Delta S^{o} < 0$
- e. $E^{\circ}_{cell} < 0$
- 3. In a spontaneous electrochemical voltaic cell, which of the following is *true*?
 - a. The cell potential is zero
 - b. Oxidation occurs at the cathode
 - c. Electrons flow from the cathode to the anode
 - d. Cations flow through the salt bridge from the cathode to the anode
 - e. The metal cathode gains mass as the cell reaction proceeds
- 4. For a spontaneous redox reaction, which of the following is *false*?
 - a. Oxidation is the process of losing electrons
 - b. Gaining electrons is reduction
 - c. Electrons appear on the left side of the oxidation half reaction
 - d. Water molecules are added to balance any extra oxygen atoms
 - e. ΔG is negative.
- 5. How are the change in Gibb's Free Energy and the equilibrium constant for a reaction related?
 - a. As K approaches zero, ΔG approaches zero
 - b. They're not.
 - c. The value of ΔG is equal to (-logK)
 - d. As ΔG gets more positive, K approaches 1
 - e. As ΔG gets more negative, K gets very large

Problems:

6. The solubility product constant (K_{sp}) for barium nitrate is 4.64x10⁻³ at 25°C. What is the concentration of nitrate ions in a saturated solution of barium nitrate at 25°C? (10pts)

		$Ba(NO_3)_2(s) \Leftrightarrow$	$Ba^{+2}(aq) +$	$2 \text{ NO}_3^{-1}(\text{aq})$				
[] _{initi}	al	XXXX	0 M	0 M				
Δ[]		XXXX	+ x M	+ 2x M				
[]equilib	rium	XXXX	x M	2x M				
$K_{sp} = [Ba^{+2}]^{1}[NO_{3}^{-1}]^{2} = (x)(2x)^{2} = 4x^{3} = 4.64x10^{-3}$								
x = 0.105								
	$[NO_3^{-1}] = 2x = 2(0.105M) = 0.210M$							

7. Give the oxidation number for each atom in the following formulas. (10pts each formula)

K_2SO_3					
$K \rightarrow Ox\# = +1$ $S \rightarrow Ox\# = +4$ $O \rightarrow Ox\# = -2$					

HOCH ₂ CH ₂ NH ₂	
H → Ov# – +1	
$C \rightarrow O_{x} = 1$	
$C \neq 0x \# = -1$	
$0 \rightarrow 0x = -2$	
$N \rightarrow Ox \# = -3$	

 For each of the following pairs of half reactions, predict which would have the more positive standard reduction potential (easier to reduce, harder to oxidize). Explain your prediction. (10pts each) SIS⁻² vs SelSe⁻²

"More positive standard reduction potential" means that the substance is more likely to be reduced, more likely to gain electrons. Because S is smaller than Se (but they're in the same column of the Periodic Table so they should have the same valence electron configuration), the nucleus of S is less shielded, so it should attract electrons more strongly than the nucleus of Se.

$Cs^{+1}|Cs \ vs \ K^{+1}|K$

The exact same argument would work here, but let's take this one from the other direction. Cs is larger than K, so the outermost valence electron in Cs (a 6s electron) is farther from the positive charge of the nucleus. This means that the outermost valence electron in Cs is lost more easily than the outermost valence electron in K (a 4s electron). If Cs *loses* electrons more easily than K, then it is easier to oxidize, so it should have a *lower* standard reduction potential.

9. You have combined 50.00mL of 0.794M potassium chloride solution and 50.00mL of 0.837M sodium perchlorate solution. A precipitate forms. What is the precipitate and what is the theoretical yield of the precipitate? (12pts) $K_{sp}(KClO_4) = 1.05 \times 10^{-2}; K_{sp}(NaCl) = 36$

This question is worded in a way that does not clearly ask the question I was trying to ask, so it was (partially) thrown out.

Because the K_{sp} of KClO₄ is lower than the K_{sp} of NaCl, the first thing to precipitate should have been KClO₄(s).

Given the information in the problem, you *could* set up a K_{sp} -type equilibrium table and figure out how $[K^{+1}]$ and $[ClO_4^{-1}]$ when the system reaches equilibrium. Once you know THOSE values, you could figure out how many moles of precipitate formed, and then how many grams of precipitate formed.

10. You would like to plate some ruthenium (Atomic # = 44) onto a small piece of jewelry. If you submerge the jewelry in 0.582M Ru(NO₃)₃(aq) and pass 1.692amperes through the solution for 1.73 minutes, how many grams of Ru will have plated onto the piece of jewelry? (12 pts)

$$(1.73 \min\left(\frac{60 \text{sec}}{1 \min}\right) \left(\frac{1.692 \text{C}}{\text{sec}}\right) \left(\frac{1 \text{mole}^{-1}}{96485 \text{C}}\right) \left(\frac{1 \text{molRu}}{3 \text{mole}^{-1}}\right) \left(\frac{101.07 \text{gRu}}{1 \text{molRu}}\right) = 0.0613 \text{gRu}$$

Name: ___

11. For each of the following pairs of half-reactions/half-cells, determine the voltage of the spontaneous reaction/cell and write a balanced equation for the spontaneous reaction, identifying the oxidation and reduction half-reactions. (12pts each)

Au^{3+}	(ad) Au(s)) and Sn^{+2}	(aa)	Sn(s)
			(~~)/	~

Oxidation:	3 (Sn(s) ⇔	$\operatorname{Sn}^{+2}(\operatorname{aq}) + 2 \operatorname{e}^{-1}$)	$E^{\circ}_{ox} = +0.136V$
Reduction:	$2(3 e^{-1} + Au^{+3}(aq) \Leftrightarrow$	Au(s))	$E^{\circ}_{red} = +1.50V$
Net Rxn:	$3 \operatorname{Sn}(s) + 2 \operatorname{Au}^{+3}(aq) \Leftrightarrow$	$2 \text{ Au}(s) + 3 \text{ Sn}^{+2}(aq)$	$E^{\circ}_{cell} = +1.64V$

$Cr^{-1}(aq) Cr(s)$ and $Br_2(aq) Br^{-1}(aq) Br^{-1}$
--

Oxidation: $2 (Cr(s) \Leftrightarrow$ Reduction: $3 (2 e^{-1} + Br_2(aq) \Leftrightarrow$ Net Rxn: $2 Cr(s) + 3 Br_2(aq) \Leftrightarrow$	$Cr^{+3}(aq) + 3 e^{-1})$ 2 Br ⁻¹ (aq)) 6 Br ⁻¹ (aq) + 2 Cr ⁺³ (aq)	$E^{\circ}_{ox} = +0.743V$ $E^{\circ}_{red} = +1.065V$ $E^{\circ}_{cell} = +1.808V$
---	--	---

 $IO_{3}^{-1}(aq)|I_{2}(s)$ and $NiO_{2}(s)|Ni^{+2}(aq)$

Oxidation:	$6 \text{ H}_2 \text{O}(1) + \text{I}_2(s) \Leftrightarrow$	$2 \text{ IO}_3^{-1}(aq) + 10 \text{ e}^{-1} + 12 \text{ H}^+(aq)$	$E_{ox}^{\circ} = -1.195V$
Reduction:	5 (4 $H^+(aq)$ + 2 e^{-1} + NiO ₂ (s) \Leftrightarrow	$Ni^{+2}(aq) + 2 H_2O(l)$	$E^{\circ}_{red} = +1.678V$
Net Rxn:	$6 \text{ H}_2\text{O}(l) + 20 \text{ H}^+(aq) + \text{I}_2(s) + 5 \text{ NiO}_2(s) \Leftrightarrow$	$5 \text{ Ni}^{+2}(aq) + 2 \text{ IO}_3^{-1}(aq) + 12 \text{ H}^+(aq) + 10 \text{ H}_2\text{O}_3$	(1) $E^{\circ}_{cell} = +0.483V$
Net Rxn:	$8 \text{ H}^{+}(\text{aq}) + \text{I}_2(\text{s}) + 5 \text{ NiO}_2(\text{s}) \Leftrightarrow$	$5 \text{ Ni}^{+2}(aq) + 2 \text{ IO}_3^{-1}(aq) + 4 \text{ H}_2\text{O}(l)$	$E^{\circ}_{cell} = +0.483V$

12. What is the expected cell potential of the spontaneous voltaic cell constructed from a 0.882M Co⁺³(aq)|Co(s) half cell and a 1.518M Ag⁺(aq)|Ag(s) half cell at 25°C? (15pts)

$$3 \text{ Ag(s)} + \text{Co}^{+3}(\text{aq}) \iff \text{Co}(s) + 3 \text{ Ag}^{+1}(\text{aq}) \qquad \text{E}^{\circ}_{\text{cell}} = +0.8324 \text{V}$$

Since this cell is not at standard conditions (1M all reactants and products), we can use the Nernst equation to calculate a non-standard E_{cell} . {Note the lack of "o" on that...}

$$E_{cell} = E_{cell}^{o} - \left(\frac{RT}{nF}\right) ln \left(\frac{\left[Ag^{+1}\right]^{3}}{\left[Co^{+3}\right]}\right) = (+0.8324V) - \left(\frac{(8.314\frac{J}{mol\bullet K})(298.15K)}{\left(\frac{3mole^{-1}}{1\,molrxn}\right)\left(\frac{96485J}{V\bullet mole^{-1}}\right)}\right) ln \left(\frac{(1.518)^{3}}{(0.882)}\right) = +0.8206V$$

Standard Reduction Potentials at 25°C:

Half cell	E ^o _{red} (volts)	Half cell	E ^o _{red} (volts)
Au ⁺³ Au	+1.50	$IO_3^{-1} I_2$	+1.195
Sn ⁺² Sn	-0.136	NiO ₂ Ni ⁺²	+1.678
Cr ⁺³ Cr	-0.743	Co ⁺³ Co	+1.632
$Br_2 Br^{-1}$	+1.065	Ag ⁺¹ Ag	+0.7996
Ru ⁺³ Ru	+1.052		