Fourth Hour Exam **5.111**

Write your name and your TA's name below**. Do not open the exam until the start of the exam is announced.** The exam is closed notes and closed book.

1. Read each part of each problem carefully and thoroughly.
2. Show your work. Indicate units. Use correct significant figures.
3. Make your dots on Lewis structures clearly visible.
4. If you don't understand what the problem is requesting, raise your hand and a proctor will come to your desk.
5. Physical constants, formulas and a periodic table are given on the last page. You may detach this page **once the exam has started**.

TRANSITION METALS	1. (32 points)
	2. (10 points)
CHEMICAL KINETICS	3. (16 points)
NUCLEAR KINETICS	4. (10 points)
OXIDATION REDUCTION	5. (10 points)
	6. (10 points)
	7. (12 points)

Total (100 points) ________________________

Name ______________________________

TA ______________________________

1. TRANSITION METALS (32 points total)

(a) (3 points) Calculate the d-count for Fe^{3+}

(b) (11 points) For Fe^{3+}, **(i)** in the appropriate places below, draw crystal field splitting diagrams with electrons to show orbital occupancies in both weak and strong **octahedral fields**. Label the diagrams (**ii**) with the names of the d-orbitals, and (**iii**) with the appropriate orbital sets e_g and t_{2g} designators.

Weak Field Octahedral Diagram **Strong Field Octahedral Diagram**

c) (6 points) Fill in the blanks below based on your diagrams in part (b).

Answer for Weak Field Diagram		**Answer for Strong Field Diagram**
(i)	system is ________ spin	system is _______ spin
(ii)	# unpaired electrons is ______	# of unpaired electrons is _______
(iii)	d^n electron configuration _______	d^n electron configuration ________

(d) (3 points) Calculate the crystal field stabilization energy (CFSE) for **high spin** Fe^{3+}. Do not include pairing energy.

(e) (3 points) Calculate the crystal field stabilization energy (CFSE) for **low spin** Fe^{3+}. Do not include pairing energy.

(f) (6 points) Calculate the octahedral crystal field splitting energy in **kJ/mol** for an Fe^{3+} complex that absorbs light most intensely at 700. nm. Show your work.

2. TRANSITION METALS (10 points total)

(**a**) (6 points) Draw d-orbitals, d_{z^2} and d_{yz} on top of the diagrams below.

draw d_{z^2} here

draw d_{yz} here

(**b**) (4 points) Predict the relative energies of just these two d-orbitals for the linear molecule drawn along the Z-axis. Explain your reasoning.

3. CHEMICAL KINETICS (16 points total)

The following data were obtained for the reaction O_2 (*g*) + 2NO (*g*) → $2NO_2$ (*g*). Initial concentrations, mol•L^{-1}

Experiment	$[O_2]_0$	$[NO]_0$	Initial rates, mol•L^{-1}•s^{-1}
1	1.10×10^{-2}	1.30×10^{-2}	3.21×10^{-3}
2	2.20×10^{-2}	1.30×10^{-2}	6.40×10^{-3}
3	1.10×10^{-2}	2.60×10^{-2}	12.8×10^{-3}

(a) (3 points) Determine the order of the reaction with respect to $[O_2]$. No need to show work.

(b) (3 points) Determine the order of the reaction with respect to [NO]. No need to show work.

(c) (3 points) Write the rate law for the overall reaction. No need to show work.

(d) (3 points) Determine the order of the overall reaction. No need to show work.

(e) (4 points) Calculate the rate constant k (the value and the units). Show your work.

4. NUCLEAR CHEMISTRY (10 points)

The activity of a strontium-90 source is 3.0×10^{14} Bq and its half-life is 28.1 years. Calculate the activity in **Bq** after 75.0 years have passed. Show your work.

5. OXIDATION REDUCTION (10 points)

(a) (6 points) Balance in **BASIC** solution the following skeletal equation by using oxidation and reduction half-reactions: $Pb(OH)_4^{2-}$ (*aq*) + ClO^- (*aq*) → PbO_2 (*s*) + Cl^- (*aq*)

(b) (4 points) The oxidizing agent is _________________and the reducing agent is _______________

6. OXIDATION-REDUCTION (10 points)

For the following reagents under standard conditions: Au (*s*), Cl_2 (*g*), Pb (*s*), Sn (*s*), Ni (*s*), Cd (s), Zn (*s*), Au^+ (*aq*), Cl^- *(aq),* Pb^{2+} (*aq*), Sn^{2+} (*aq*), Ni^{2+} (*aq*), Zn^{2+} (*aq*)

Standard Reduction Potentials at 25°C

Half-Reactions	*E*°(volts)
Au^+ (*aq*)+ e^- ⇒ Au (*s*)	1.69
Cl_2 (*g*) + $2e^-$ → $2Cl^-$ (*aq*)	1.36
$2H^+$ (*aq*) + $2e^-$ ⇒ H_2 (*g*)	0
Pb^{2+}(*aq*) + 2 e^- ⇒ Pb (*s*)	-0.13
Sn^{2+}(*aq*) + 2 e^- ⇒ Sn (*s*)	-0.15
Ni^{2+}(*aq*) + 2 e^- ⇒ Ni (*s*)	-0.26
Cd^{2+}(*aq*) + 2 e^- ⇒ Cd (*s*)	-0.40
Zn^{2+}(*aq*) + $2e^-$ ⇒ Zn (*s*)	-0.76

(a) (3 points) State which reagent is the strongest oxidizing agent.

(b) (3 points) State which reagent is the strongest reducing agent.

(c) (4 points) State which reagent(s) will reduce Pb^{2+} (*aq*) while leaving Cd^{2+} (*aq*) unreacted.

7. OXIDATION-REDUCTION (12 points)

A galvanic cell is constructed using the following half-reactions

Half-Reactions	*E*°(volts) at 25°C
$Pb^{2+}(aq) + 2\ e^- \Rightarrow Pb\ (s)$	- 0.13
$Cr^{3+}\ (aq) + e^- \Rightarrow Cr^{2+}\ (aq)$	- 0.42

Calculate the initial voltage generated by the cell at 25℃ if the initial concentration of Pb^{2+} (*aq*) is 0.15 M, Cr^{2+}(*aq*) is 0.20 M, and Cr^{3+} (*aq*) is 0.0030 M. Show your work.

1 IA	2 IIA	3 IIIB	4 IVB	5 VB	6 VIB	7 VIIB	8	9 VIIIB	10	11 IB	12 IIB	13 IIIA	14 IVA	15 VA	16 VIA	17 VIIA	18[a] VIIIA b
The Active Metals																	Noble Gases
1 H 1.008												The Nonmetals					2 He 4.003
3 Li 6.941	4 Be 9.012											5 B 10.81	6 C 12.011	7 N 14.007	8 O 15.999	9 F 18.998	10 Ne 20.179
11 Na 22.990	12 Mg 24.305	Transition Elements										13 Al 26.982	14 Si 28.086	15 P 30.974	16 S 32.06	17 Cl 35.453	18 Ar 39.948
19 K 39.098	20 Ca 40.08	21 Sc 44.956	22 Ti 47.88	23 V 50.942	24 Cr 51.996	25 Mn 54.938	26 Fe 55.847	27 Co 58.933	28 Ni 58.69	29 Cu 63.546	30 Zn 65.38	31 Ga 69.72	32 Ge 72.59	33 As 74.922	34 Se 78.96	35 Br 79.904	36 Kr 83.80
37 Rb 85.468	38 Sr 87.62	39 Y 88.906	40 Zr 91.224	41 Nb 92.906	42 Mo 95.94	43 Tc (98)	44 Ru 101.07	45 Rh 102.906	46 Pd 106.42	47 Ag 107.868	48 Cd 112.41	49 In 114.82	50 Sn 118.69	51 Sb 121.75	52 Te 127.60	53 I 126.904	54 Xe 131.29
55 Cs 132.905	56 Ba 137.33	57 La 138.905	* 72 Hf 178.49	73 Ta 180.948	74 W 183.85	75 Re 186.21	76 Os 190.2	77 Ir 192.22	78 Pt 195.08	79 Au 196.966	80 Hg 200.59	81 Tl 204.38	82 Pb 207.2	83 Bi 208.98	84 Po (209)	85 At (210)	86 Rn (222)
87 Fr (223)	88 Ra 226.025	89 Ac 227.028	† 104 Unq (261)	105 Unp (262)	106 Unh (263)												

Inner Transition Metals

* Lanthanides	58 Ce 140.12	59 Pr 140.908	60 Nd 144.24	61 Pm (145)	62 Sm 150.36	63 Eu 151.96	64 Gd 157.25	65 Tb 158.925	66 Dy 162.50	67 Ho 164.930	68 Er 167.26	69 Tm 168.934	70 Yb 173.04	71 Lu 174.967
† Actinides	90 Th 232.038	91 Pa 231.036	92 U 238.029	93 Np 237.048	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)

Equation Sheet Exam 4

$c = 2.9979 \times 10^{8}$ m/s

$h = 6.6261 \times 10^{-34}$ J s

$N_A = 6.02214 \times 10^{23}$ mol^{-1}

R = 8.314 J/(K mol)

1 eV = 1.60218×10^{-19} J

$K_w = 1.00 \times 10^{-14}$ at 25.0°C

14.00 = pH + pOH at 25.0°C

$\Im$ (Faraday's constant) = 96,485 C mol^{-1}

Electromagnetic Spectrum:
Violet ~ 400-430 nm Blue ~ 431-490 nm
Green ~ 491-560 nm
Yellow ~ 561-580 nm Orange ~ 581-620 nm
Red ~ 621-700 nm

Complementary Colors: red/green, blue/orange, yellow/violet

$I^- < Br^- < Cl^-$ (weak field ligands)
$< F^- < OH^- < H_2O$ (intermediate)
$< NH_3 < CO < CN^-$ (strong field ligands)

1 Coulomb • Volt = 1 Joule

1 Bq = 1 nuclei/sec

1A = 1C/s   1W = 1 J/s

ln = 2.3025851log

1 J = 1 kgm^{2}s^{-2}

$x = [-b \pm (b^2 - 4ac)^{1/2}]/2a$

$ax^2 + bx + c = 0$

$E = h\nu = hc/\lambda$

$c = \nu\lambda$

$\Delta G = \Delta H - T\Delta S$

$\Delta G = \Delta G° + RT \ln Q$

$\Delta G° = -RT \ln K$

$\Delta G = RT \ln Q/K$

$\ln (K_2/K_1) = -(\Delta H°/R)(1/T_2 - 1/T_1)$

$pH \approx pK_a - \log (HA/A^-)$

$pH = -\log [H_3O^+]$ $pOH = -\log [OH^-]$

$K_w = K_a K_b$ $pK = -\log K$

$Q = It$

$\Delta G°_{cell} = -(n)(\Im)\ \Delta E°_{cell}$

$\Delta E°(\text{cell}) = E°(\text{cathode}) - E°(\text{anode})$

$\Delta E° = E°(\text{reduction}) - E°(\text{oxidation})$

$\Delta E_{cell} = E°_{cell} - (RT/n\Im)\ln Q$

$RT/\Im = 0.025693$ V at 25.0 °C
$\Im/RT = 38.921$ V^{-1} at 25.0 °C

$\Delta E_{cell} = E°_{cell} - [(0.025693\ V)(\ln Q)/n]$ at 25.0°C

$\Delta E_{cell} = E°_{cell} - [(0.0592\ V)(\log Q)/n]$ at 25.0°C

$\ln K = (n\Im/RT)\ \Delta E°$

$A = A_o e^{-kt}$

$N = N_o e^{-kt}$

$A = kN$

$[A] = [A]_o e^{-kt}$ $t_{1/2} = \ln 2 / k$

$1/[A] = 1/[A]_o + kt$ $t_{1/2} = 1 / k[A]_o$