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 Answer Key

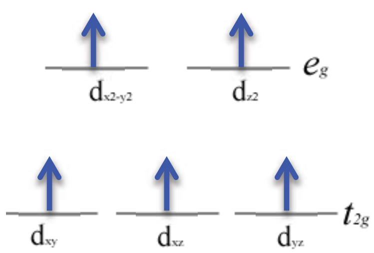
TA ________________

1. TRANSITION METALS (32 points total)

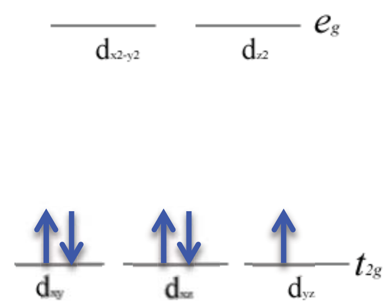
(a) (3 points) Calculate the d-count for Fe^{3+}

5

(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

(i) system is high spin
(ii) # unpaired electrons is 5
(iii) d^n electron configuration $t_{2g}^{3}e_g^{2}$

Answer for Strong Field Diagram

system is low spin
# of unpaired electrons is 1
d^n electron configuration t_{2g}^{5}

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

0

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

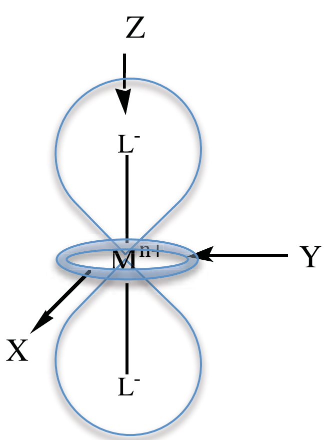
$-2\Delta_o$

(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.

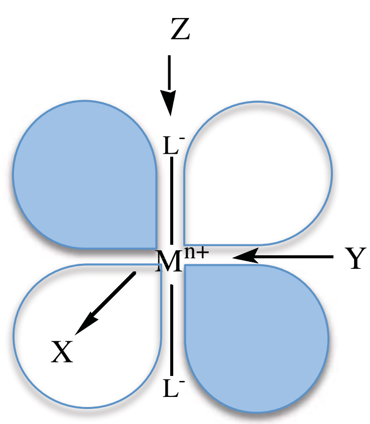
Δ_o = 171 kJ/mol

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.

d_{z^2} is much more destabilized than d_{yz}. Ligands right along z will repel d_{z^2} orbitals since these orbitals are on axis. d_{yz} is 45° off axis, so repulsion is less.

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.

First order

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

Second order

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

Rate = $k[O_2][NO]^2$

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

3

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

k = **1730** $\boldsymbol{M^{-2}s^{-1}}$

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.

$A=4.7 \times 10^{13}$ Bq

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*)

$Pb(OH)_4^{2-} + ClO^-$ $PbO_2 + H_2O + Cl^- + 2OH^-$

(b) (4 points) The oxidizing agent is Cl^+ or ClO^- and the reducing agent is Pb^{2+} or $Pb(OH)_4^{2-}$

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.

Au^+

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

Zn (s)

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

Sn(s)
Ni (s)

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.

E = 0.37 V