

Write your name and your TA's name below. **Do not open the exam until the start of the exam is announced.** 1) Read each part of a problem thoroughly. Many of a problem's latter parts can be solved without having solved earlier parts. If you need a numerical result that you were not successful in obtaining for the execution of a latter part, make a physically reasonable approximation for that quantity. 2) Show all steps of a calculation and indicate all values used to obtain your quantitative result. Significant figure usage must be correct. 3) If you don't understand what the problem is requesting, raise your hand. 4) Physical constants, formulas and a periodic table are given on the last 2 pages. You may detach these pages **once the exam has started.**

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	TOTAL	(300 points) _____

TA \_\_\_\_\_ Name \_\_\_\_\_

**1. TRANSITION METALS (35 points total)****(a)** (3 points) Calculate the d-count for  $\text{Fe}^{2+}$ 

$$8 - 2 = \mathbf{d^6} \quad \text{all or nothing}$$

**(b)** (14 points) Draw the octahedral crystal field splitting diagrams for  $\text{Fe}^{2+}$  with both weak and strong octahedral fields. Label the diagrams weak and strong field, high spin and low spin, give the names of the d-orbitals, and label the appropriate orbital sets  $e_g$  and  $t_{2g}$ .

- (a) +3 points PER diagram for: correct electron distribution and weak/strong high/low spin labeling  
 (b) +3 total for  $e_g$  and  $t_{2g}$  labels  
 (c) +5 total for correct d orbital labels

**(c)** (4 points) Calculate the crystal field stabilization energy (CFSE) for **high spin**  $\text{Fe}^{2+}$ . Do not include pairing energy.

$$\text{CFSE} = 4(-2/5 \Delta_o) + 2(+3/5 \Delta_o) = \mathbf{-2/5 \Delta_o} \quad +4$$

-2 if missing  $\Delta_o$  label  
 -1 for a math error

**(d)** (4 points) Calculate the crystal field stabilization energy (CFSE) for **low spin**  $\text{Fe}^{2+}$ . Do not include pairing energy.

$$\text{CFSE} = 6(-2/5 \Delta_o) = \mathbf{-12/5 \Delta_o} \quad +4$$

-2 if missing  $\Delta_o$  label  
 -1 for a math error

(e) (4 points) If the  $\text{Fe}^{2+}$  coordination complex is  $[\text{Fe}(\text{CN})_6]^{4-}$ , state whether you expect the complex to be high spin or low spin? Explain your answer.

**Low spin**

+2 for correct answer

**$\text{CN}^-$  is a strong field ligand**

+2 for explanation

(f) (6 points) Calculate the octahedral crystal field splitting energy in **kJ/mol** for  $[\text{Fe}(\text{CN})_6]^{4-}$ , if the wavelength of the most intensely absorbed light is 305 nm.

$$\Delta_o = h\nu \quad \nu = c/\lambda \quad \Delta_o = hc/\lambda$$

$$\Delta_o = 6.6261 \times 10^{-34} \text{ Js} \left( \frac{2.9979 \times 10^8 \text{ m/s}}{305 \times 10^{-9} \text{ m}} \right) \quad \left. \vphantom{\Delta_o} \right\} +4$$

$$\Delta_o = 6.513 \times 10^{-19} \text{ J}$$

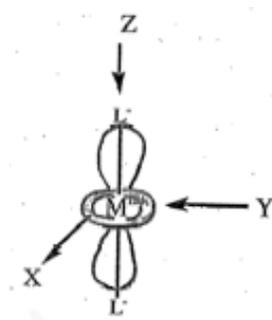
$$6.513 \times 10^{-19} \text{ J} \times \frac{1 \text{ kJ}}{1000 \text{ J}} \times 6.02214 \times 10^{23} \frac{\text{molecules}}{\text{mol}} = 392 \text{ kJ/mol} \quad \left. \vphantom{\Delta_o} \right\} +2$$

-1 per math error, -1 if units are not included

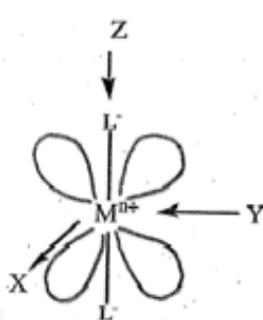
## 2. TRANSITION METALS (10 points total)

(i) Draw  $d_{z^2}$  and  $d_{yz}$  on top of the diagrams below, and (ii) predict the relative energies of just these two d-orbitals for the linear molecule drawn along the Z-axis. Explain your reasoning.

draw  $d_{z^2}$  here



draw  $d_{yz}$  here



**$d_{z^2}$  higher in energy;**

orbitals and ligands on axis; ligands pointing directly toward  $d_{z^2}$  orbitals

+1 for correct answer

+2 for correct explanation

**$d_{yz}$  is  $45^\circ$  off axis; ligands are not pointing directly toward  $d_{yz}$ , so less repulsion (lower in energy)**

+1 for correct answer

+2 for correct explanation

+ 2 for  $d_{z^2}$  drawing

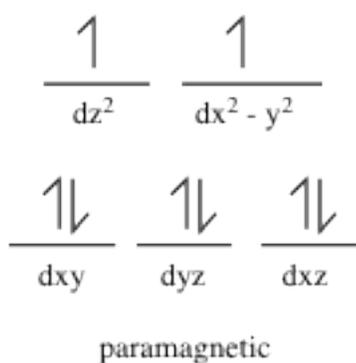
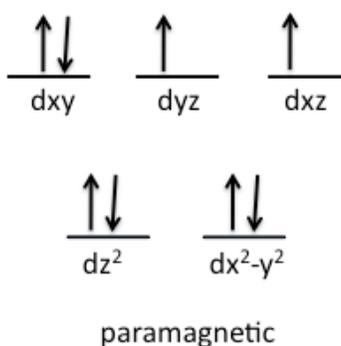
+ 2 for  $d_{yz}$  drawing

(orbital shading is not required, but it is ok if included)

**3. TRANSITION METALS (16 points total)**

$\text{Ni}^{2+}$  in a coordination complex is paramagnetic. Draw the crystal field splitting diagrams for an octahedral crystal field and a tetrahedral crystal field, labeling the d-orbitals. State below each diagram whether the geometry is consistent with a paramagnetic species.

$$d \text{ count} = 10 - 2 = 8$$

**OCTAHEDRAL DIAGRAM****TETRAHEDRAL DIAGRAM****Grading:**

(a) 7 points per diagram; +1 for each d orbital label, +2 for correct electron configuration

(b) 1 point each (+2 total) for writing “paramagnetic” OR “consistent”

*note: if a student labeled orbital sets with  $e_g$ ,  $t_{2g}$ ,  $e$ ,  $t_2$  instead of labeling each d orbital, give 1 point for each correct label.*

**4. CHEMICAL KINETICS (18 points total)**

The following data were obtained for the reaction  $A + B + C \rightarrow \text{products}$ .

Experiments	Initial concentrations, mol•L <sup>-1</sup>			Initial rates, mol•L <sup>-1</sup> •s <sup>-1</sup>
	[A] <sub>0</sub>	[B] <sub>0</sub>	[C] <sub>0</sub>	
1	0.10	0.10	0.10	$1.2 \times 10^{-3}$
2	0.20	0.10	0.10	$2.4 \times 10^{-3}$
3	0.10	0.30	0.10	$3.5 \times 10^{-3}$
4	0.20	0.10	0.15	$5.5 \times 10^{-3}$

(a) (3 points) Determine the order of the reaction with respect to A

$$\frac{0.20}{0.10} \quad \frac{2.4 \times 10^{-3}}{1.2 \times 10^{-3}} \quad \text{first} \quad +3 \text{ (all or nothing)}$$

$$2 \quad 2$$

(b) (3 points) Determine the order of the reaction with respect to B

$$\frac{0.30}{0.10} \quad \frac{3.5 \times 10^{-3}}{1.2 \times 10^{-3}} \quad \text{first} \quad +3 \text{ (all or nothing)}$$

$$3 \quad 3$$

(c) (3 points) Determine the order of the reaction with respect to C

$$\frac{0.15}{0.10} \quad \frac{5.5 \times 10^{-3}}{2.4 \times 10^{-3}} \quad 1.5x = 2.3 \quad \text{second} \quad +3 \text{ (all or nothing)}$$

$$x = 2$$

$$1.5 \quad 2.3$$

(d) (3 points) Write the rate law for the overall reaction.

$$\text{rate} = k[A][B][C]^2 \quad +3 \text{ (give full credit for an incorrect answer consistent with a mistake above)}$$

-2 if missing k

(e) (3 points) Determine the order of the overall reaction.

$$4 \quad +3 \text{ (give full credit for an incorrect answer consistent with a mistake above)}$$

(f) (3 points) Calculate the rate constant k

$$\text{rate} = 5.5 \times 10^{-3} \text{ M/s} = k[0.20][0.10][0.15]^2 \quad +3 \text{ for correct answer}$$

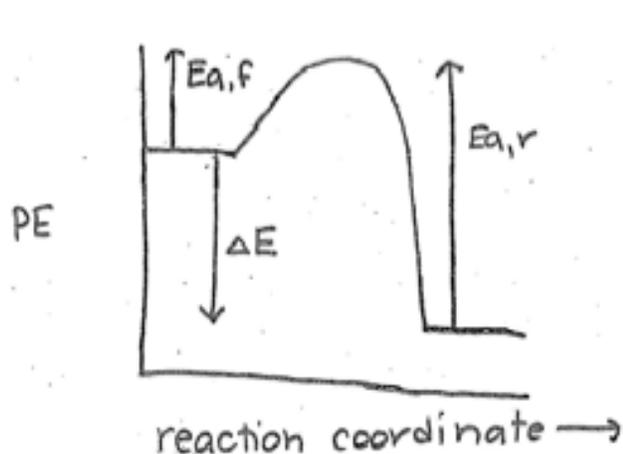
$$k = \frac{5.5 \times 10^{-3} \text{ M/s}}{0.00045 \text{ M}^4} = 12 \text{ M}^{-3}\text{s}^{-1}$$

-1 per math error, -2 for wrong/no units

**5. CHEMICAL KINETICS AND CHEMICAL EQUILIBRIUM (32 points total)**

For a reversible, one step reaction  $2A \xrightleftharpoons[k_{-1}]{k_1} B + C$ , the rate constant for the forward reaction is  $406 \text{ M}^{-1} \text{ min}^{-1}$  and the rate constant for the reverse reaction is  $244 \text{ M}^{-1} \text{ min}^{-1}$ . The activation energy for the forward reaction is  $26.2 \text{ kJ mol}^{-1}$  and that for the reverse direction is  $42.4 \text{ kJ mol}^{-1}$ .

(a) (5 points) Draw a reaction coordinate diagram (Potential energy versus Reaction coordinate) for this reaction and state whether the reaction is endothermic or exothermic. Label (i)  $\Delta E$ , (ii)  $E_{a,f}$ , (iii)  $E_{a,r}$ .



+3 for correct diagram, +2 for writing “exothermic”

(b) (5 points) Calculate  $\Delta E$  for this reaction ( $2A \xrightleftharpoons[k_{-1}]{k_1} B + C$ ). Show your work.

$$\Delta E = E_{a,f} - E_{a,r}$$

$$26.2 \text{ kJ/mol} - 42.4 \text{ kJ/mol} = \mathbf{-16.2 \text{ kJ/mol}} \quad +5$$

-1 per math error, -2 for no units, -1 for incorrect SF  
zero points total for an answer of +16.2 kJ/mol

(c) (5 points) Calculate the equilibrium constant for this reaction ( $2A \xrightleftharpoons[k_{-1}]{k_1} B + C$ ). Show your work.

$$K = \frac{k_1}{k_{-1}} = \frac{406 \text{ M}^{-1} \text{ min}^{-1}}{244 \text{ M}^{-1} \text{ min}^{-1}} = \mathbf{1.66} \quad +5$$

-1 per math error, -1 for units, -1 for incorrect SF

(d) (6 points) Predict the effect of raising the temperature on the forward rate constant, and compare it to the effect of raising the temperature on the reverse rate constant. Explain your answer.

Both  $k$ 's will increase because more molecules will have the energy necessary to overcome the  $E_a$  barrier.  $k_{\text{reverse}}$  will increase more because the  $E_{a,r}$  barrier is higher.

+ 3 for writing that both increase

+3 for writing that  $k_{\text{reverse}}$  will increase more than  $k_{\text{forward}}$

(-6 if write that either will decrease)

(e) (5 points) Predict the effect of raising the temperature on the equilibrium constant. Explain your answer.

**K will decrease.**

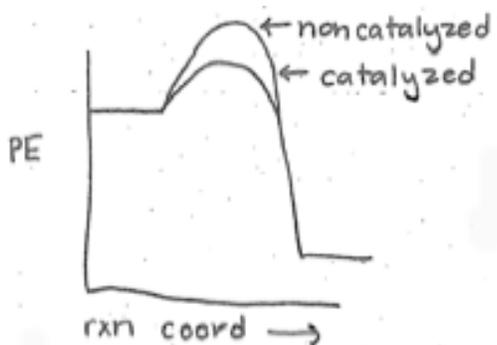
+2 for correct answer

Le Chatelier's ~ for exothermic reaction, shift to reactant (absorb heat) +3 for explanation

OR

K will decrease since  $k_{-1}$  (reverse) increases more than  $k_1$  (forward) and  $K = \frac{k_1}{k_{-1}}$

(f) (6 points) Draw a single reaction coordinate diagram (Potential energy versus Reaction coordinate), that includes both a catalyzed and a noncatalyzed reaction trace, indicating the effect of adding a catalyst to the reaction. Briefly explain how a catalyst works.



+3 points for diagram

+3 points for one of the following explanations:

- catalysts lower  $E_a$  and stabilize transition state OR
- stabilize activated complex OR
- speed up reaction without being consumed

**6. ENZYME KINETICS (7 points)**

Enzyme penicillinase degrades antibiotic penicillin leading to bacterial resistance. The Michaelis-Menten constants for this enzyme and substrate are  $K_m = 5 \times 10^{-5} \text{ mol/L}$  and  $k_2 = 2 \times 10^3 \text{ s}^{-1}$ .

(a) (4 points) Calculate the maximum rate of this reaction if the total enzyme concentration is  $7 \times 10^{-5} \text{ M}$ .

$$V_{\max} = k_2[E_0] = (2 \times 10^3 \text{ s}^{-1})(7 \times 10^{-5} \text{ M}) = 1 \times 10^{-1} \text{ M s}^{-1}$$

-1 MATH

-1 incorrect SF

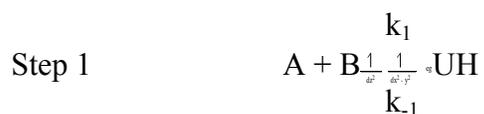
-1 units

(b) (3 points) Find the substrate concentration for which the rate will be half of that calculated in part (a).

**$5 \times 10^{-5} \text{ M}$**  (all or nothing)

**7. CHEMICAL KINETICS (12 points total)**

Consider the formation of a DNA double helix from strands A and B. In the first step, strands A and B form an unstable helix (UH), and in step 2, the unstable helix (UH) converts to a stable helix (SH).



(a) (2 point) Indicate the molecularity of the first step.

Bimolecular (all or nothing)

(b) (2 point) Indicate the molecularity of the second step.

unimolecular (all or nothing)

(c) (8 points) Write the rate law for the formation of the stable helix (SH) assuming the equilibrium between A+B and UH is fast. Be sure to eliminate intermediates from the rate expression. Show all work for full credit.

$$\text{Rate} = k_2 [\text{UH}]$$



Intermediate

$$k_1 [\text{A}][\text{B}] = k_{-1} [\text{UH}]$$

$$[\text{UH}] = k_1 [\text{A}][\text{B}]$$

$$[\text{UH}] = \frac{k_1 [\text{A}][\text{B}]}{k_{-1}}$$

$$\text{rate} = \frac{k_1 k_2 [\text{A}][\text{B}]}{k_{-1}}$$

**8. NUCLEAR CHEMISTRY (10 points)**

The activity of a strontium-90 source is  $3.0 \times 10^{14}$  Bq and its half-life is 28.1 years. Calculate the activity after 75.0 years have passed. Show all work.

$$\text{FYI } (365 \text{ days/yr}) \times (24 \text{ hr/day}) \times (3600 \text{ s/hr}) = 31536000 \text{ s/yr}$$

$$75.0 \text{ yr} \times (1 \text{ yr}/31536000 \text{ s}) = 2.365 \times 10^9 \text{ s}$$

**Find k (+4)**

$$t_{1/2} = \ln 2/k = \ln 2/(28.1 \text{ yr}) = 0.02466 \text{ yr}^{-1}$$

**or**

$$t_{1/2} = \ln 2/k = \ln 2/(28.1 \text{ yr} \times 1/31536000 \text{ s}) = 7.819 \times 10^{-10} \text{ s}^{-1}$$

**Find A (+6)**

$$A = A_0 e^{-kt}$$

$$A = 3.0 \times 10^{14} \text{ Bq} e^{-(0.02466/\text{yr})(75.0 \text{ yr})} \quad \text{or} \quad A = 3.0 \times 10^{14} \text{ Bq} e^{-(7.819 \times 10^{-10}/\text{s})(2.365 \times 10^9 \text{ s})}$$

$$A = 3.0 \times 10^{14} \text{ Bq} e^{-1.849}$$

$$A = 3.0 \times 10^{14} \text{ Bq} (0.1572)$$

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

**-1 MATH**

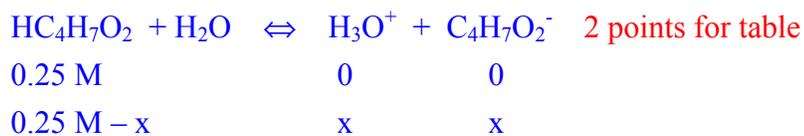
**-1 incorrect SF**

**- 1 incorrect units**

**9. ACID-BASE EQUILIBRIA (10 points)**

A 0.250 M aqueous solution of  $\text{HC}_4\text{H}_7\text{O}_2$  is found to have a pH of 2.72. Determine  $K_a$  for butyric acid to two significant figures. Show all work.

weak acid problem    1 point back if the write this



$$\text{pH} = -\log[\text{H}_3\text{O}^+]$$

$$2.72 = -\log[\text{H}_3\text{O}^+]$$

$$[\text{H}_3\text{O}^+] = 0.001905$$

4 points

$$K_a = \frac{[\text{H}_3\text{O}^+][\text{C}_4\text{H}_7\text{O}_2^-]}{[\text{HC}_4\text{H}_7\text{O}_2]}$$

$$K_a = \frac{(0.001905)^2}{(0.25 - 0.001905)} = \frac{3.63 \times 10^{-6}}{0.24809} = 1.46 \times 10^{-5}$$

$$K_a = 1.5 \times 10^{-5}$$

3 points

-1 per math/copying error, -1 for SF

Maximum of 4/10 if do wrong type of problem

**10. ACID-BASE EQUILIBRIA (25 points)**

Answer parts a-c for the titration of 100.00 mL of weak acid HCOOH ( $K_a = 1.8 \times 10^{-4}$ ) with 0.0750 M strong base NaOH at 25.0°C.

(a) (5 points) Calculate the number of moles of HCOOH in 100.00 mL of an aqueous solution if it requires 15.90 mL of 0.0750 M NaOH to titrate it to the equivalence (stoichiometric) point.

$$0.01590 \text{ L} \times 0.0750 \text{ mol/L} = 0.0011925 \text{ mol}$$

$$0.00119 \text{ mol} \text{ OR } 1.19 \times 10^{-3} \text{ mol} \quad +5$$

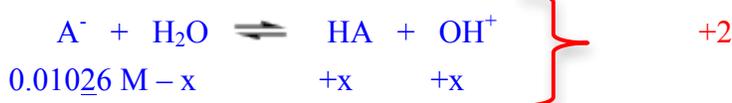
-1 math/rounding error, -1 SF, -1 units

(b) (12 points) Calculate the pH at the equivalence (stoichiometric) point. Show all work. Check any assumption you make for full credit.

weak base problem +1 back if they write this

0.00119 mol of  $A^-$  formed

$$\frac{0.00119 \text{ mol}}{100.00 + 15.90 \text{ mL}} = 0.01026 \text{ M}$$



$$K_b = K_w/K_a = \frac{1.00 \times 10^{-14}}{1.8 \times 10^{-4}} = 5.55 \times 10^{-11} \quad +2$$

$$K_b = \frac{[HA][OH^-]}{[A^-]} = 5.55 \times 10^{-11} = \frac{x^2}{0.01026 - x} \cong \frac{x^2}{0.01026} \quad x = 7.55 \times 10^{-7} \quad +2$$

$$pOH = -\log[OH^-] = -\log(7.55 \times 10^{-7}) = 6.12$$

$$pH = 14.00 - 6.12 = 7.88$$

(Give 3 points back if answer is  $< 7$ , but they note that the answer must be  $> 7$ )

check assumption:

$$((7.55 \times 10^{-7})/(0.01026)) \times 100\% = 0.0076\% \quad +1 \text{ for checking assumption}$$

-1 per math/copying error, -1 SF (maximum of 5/12 if try to do wrong type of problem)

(c) (8 points) Calculate the pH **past** the equivalence (stoichiometric) point when 1.0 mL of extra NaOH has been added. Show all work.

Strong base in water problem

+1 back if write

$$1.0 \times 10^{-3} \text{ L} \times 0.0750 \text{ M} = 0.000075 \text{ mol OH}^-$$

+2

$$\frac{0.000075 \text{ mol}}{115.90 \times 10^{-3} \text{ L}} = 0.000642 \text{ M}$$

+3 (-3 if vol is wrong)

$$\text{pOH} = -\log [0.000642] = 3.192$$

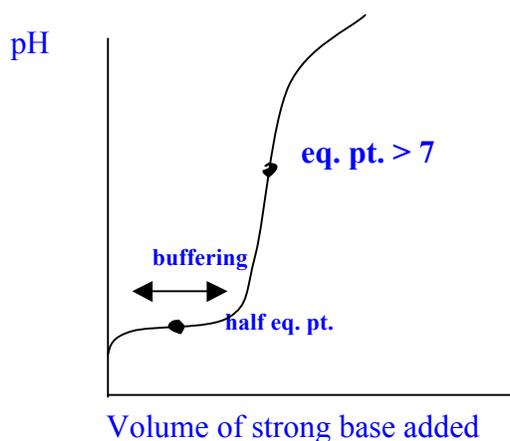
$$\text{pH} = 14.00 - 3.182 = 10.81$$

+3

(Give 3 points back if answer is  $< 7$ , but they note that the answer must be  $> 7$ )

### 11. ACID-BASE EQUILIBRIA (5 points)

Draw a titration curve for a weak acid/strong base titration. (a) Label the axes, (b) mark the equivalence point, (c) mark the half-equivalence point, (d) mark the buffering region, and (e) indicate whether the pH at the equivalence point should be  $< 7$ ,  $= 7$ , or  $> 7$



1 point (a) Label the axes

1 point (b) mark the equivalence point

1 point (c) mark the half-equivalence point,

1 point (d) mark the buffering region

1 point (e) indicate pH at the equivalence point  $> 7$

(subtract 2 points total if draw everything perfectly for adding an acid to a base)

**12. OXIDATION-REDUCTION (10 points)**

For the following reagents under standard conditions:

$\text{Au (s)}$ ,  $\text{Cl}_2 \text{ (g)}$ ,  $\text{Pb (s)}$ ,  $\text{Sn (s)}$ ,  $\text{Ni (s)}$ ,  $\text{Cd (s)}$ ,  $\text{Zn (s)}$ ,  $\text{Au}^+ \text{ (aq)}$ ,  $\text{Cl}^- \text{ (aq)}$ ,  $\text{Pb}^{2+} \text{ (aq)}$ ,  $\text{Sn}^{2+} \text{ (aq)}$ ,  $\text{Ni}^{2+} \text{ (aq)}$ ,  $\text{Zn}^{2+} \text{ (aq)}$

Standard Reduction Potentials at 25°C

Half-Reactions	$E^\circ$ (volts)
$\text{Au}^+ \text{ (aq)} + \text{e}^- \Rightarrow \text{Au (s)}$	1.69
$\text{Cl}_2 \text{ (g)} + 2\text{e}^- \rightarrow 2\text{Cl}^- \text{ (aq)}$	0.14
$2\text{H}^+ \text{ (aq)} + 2\text{e}^- \Rightarrow \text{H}_2 \text{ (g)}$	0
$\text{Pb}^{2+} \text{ (aq)} + 2\text{e}^- \Rightarrow \text{Pb (s)}$	-0.13
$\text{Sn}^{2+} \text{ (aq)} + 2\text{e}^- \Rightarrow \text{Sn (s)}$	-0.14
$\text{Ni}^{2+} \text{ (aq)} + 2\text{e}^- \Rightarrow \text{Ni (s)}$	-0.23
$\text{Cd}^{2+} \text{ (aq)} + 2\text{e}^- \Rightarrow \text{Cd (s)}$	-0.40
$\text{Zn}^{2+} \text{ (aq)} + 2\text{e}^- \Rightarrow \text{Zn (s)}$	-0.76

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

$\text{Au}^+ \text{ (aq)}$  +3 (all or nothing)

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

$\text{Zn (s)}$  +3 (all or nothing)

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

$\text{Ni (s)}$  +2

$\text{Sn (s)}$  +2

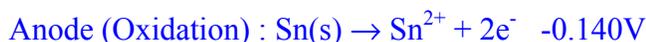
(-2 for each wrong answer with a minimum score of 0/4) (don't take off or give points for Cd (s))

**13. OXIDATION/REDUCTION REACTIONS (10 points)**

A tin electrode in 0.015 M  $\text{Sn}(\text{NO}_3)_2$  (aq) is connected to a hydrogen electrode in which the pressure of  $\text{H}_2$  is 1.0 bar. If  $\Delta E$  is 0.061 V at  $25^\circ\text{C}$ , calculate the pH at  $25^\circ\text{C}$  of the electrolyte at the hydrogen electrode to one decimal place for this galvanic cell. Show all work.

Standard Reduction Potentials at  $25^\circ\text{C}$

Half-Reactions	$E^\circ$ (volts)
$2\text{H}^+(\text{aq}) + 2\text{e}^- \Rightarrow \text{H}_2(\text{g})$	0
$\text{Sn}^{2+}(\text{aq}) + 2\text{e}^- \Rightarrow \text{Sn}(\text{s})$	-0.140



$$E^\circ_{\text{cell}} = E^\circ_{\text{cathode}} - E^\circ_{\text{anode}} = 0 - (-0.140\text{V}) = 0.140\text{ V} \quad +3 \text{ (give 0/3 for -0.140 V)}$$

$$E = E^\circ - \frac{0.0592}{n} \log(Q)$$

$$0.061\text{ V} = 0.140\text{ V} - \frac{0.0592}{2} \log(Q)$$

$$0.061\text{ V} - 0.140\text{ V} = -\frac{0.0592}{2} \log(Q) \quad +3$$

$$-0.079 = -\frac{0.0592}{2} \log(Q)$$

$$2.67 = \log(Q)$$

$$Q = 467$$

$$Q = \frac{[\text{Sn}^{2+}][\text{H}_2]}{[\text{H}^+]^2}$$

$$467 = (0.015)(1)/(x^2) \quad +3$$

$$x = [\text{H}^+] = 0.005667$$

$$\text{pH} = -\log[\text{H}^+] = 2.2 \text{ (ok for different rounding + or - 0.1)} \quad +1$$

-1 per math error, -1 SF

(if use -0.140 V for  $E^\circ_{\text{cell}}$  and get pH = -2.5, give 7/10 points)

**14. ELECTRONS AND TRENDS (35 points)**

Answers questions a-g below.

- (a) (5 points) Circle the statement about the photoelectric effect that is incorrect.
- 1) **A plot of the kinetic energy of the ejected electrons versus the frequency of the incident radiation has a slope that is equal to the value of the work function.**
  - 2) All metals have a unique work function.
  - 3) The kinetic energy of the ejected electrons does not increase with the intensity of the incident radiation.
  - 4) A plot of the kinetic energy of the ejected electrons versus the frequency of the incident radiation is linear.
- (b) (4 points) Indicate the number of nodes (both radial and angular) that are present in a 3p orbital and a 3d orbital.
- 3p: Radial: 1                  Angular: 1
- 3d: Radial: 0                  Angular: 2                  +1 each
- (c) (4 points) Circle the set of quantum numbers that could correspond to a 5f-orbital.
- 1)  $n = 5, l = 4, m = +3$
  - 2)  $n = 5, l = 3, m = +4$
  - 3)  **$n = 5, l = 3, m = -3$**
  - 4)  $n = 4, l = 3, m = +1$
  - 5)  $n = 4, l = 2, m = 0$

- (d) (6 points) Calculate the longest-wavelength line in the series for emission into the  $n = 3$  level of the hydrogen atom. Give your answers in units of nm to four significant figures.

$$\begin{aligned} \nu &= \frac{Z^2 R_H}{h} \left( \frac{1}{n_f^2} - \frac{1}{n_i^2} \right) = \frac{1^2 (2.1799 \times 10^{-18} \text{ J})}{6.6261 \times 10^{-34} \text{ J s}} \left( \frac{1}{(3)^2} - \frac{1}{(4)^2} \right) \\ &= 1.599242 \times 10^{14} \text{ s}^{-1} \\ \lambda &= \frac{c}{\nu} = \frac{2.9979 \times 10^8 \text{ m s}^{-1}}{1.599242 \times 10^{14} \text{ s}^{-1}} \\ &= 1.87458 \times 10^{-6} \text{ m} \\ &= 1874 \text{ nm} \end{aligned}$$

+4 for  $\nu$

+ 2 for  $\lambda$

-1 for math, -1 units, -1 SF

- (e) (6 points) Consider the following ground-state electronic configurations. Circle the electronic configuration that has both the highest first ionization energy and the highest electron affinity. Write the name of the corresponding atom.

1) [Ne]  $3s^2 3p^5$  (+4)

2) [Ne]  $3s^2 3p^3$

3) [Ne]  $3s^2 3p^1$

4) [Ne]  $3s^2 3p^4$

Atom is Cl (+2)

(f) (5 points) Circle the ion or element that has the largest atomic radius.

1) **S<sup>2-</sup>**

2) Cl

3) Cl<sup>-</sup>

4) K<sup>+</sup>

5) S

(g) (5 points) Circle the compound that has the bond with the most ionic character.

1) AgI

2) AgCl

3) AgF

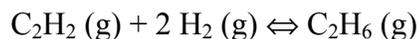
4) KCl

5) **KF**



**16. THERMOCHEMISTRY (40 points)**

Consider the following reaction:



The following may be useful.

	$\Delta H_f^\circ$ (298K)	$S^\circ$ (298K)
$\text{C}_2\text{H}_6(\text{g})$	-84.68 kJ/mol	229.60 J/(K mol)
$\text{C}_2\text{H}_2(\text{g})$	226.73 kJ/mol	200.94 J/(K mol)
$\text{H}_2(\text{g})$		130.68 J/(K mol)

Throughout this problem you may make the usual assumption that  $\Delta H^\circ$  and  $\Delta S^\circ$  are independent of temperature.

(a) (8 points) Calculate the heat of reaction ( $\Delta H_{rx}^\circ$ ). State whether the reaction is exothermic or endothermic.

Answer:

$$\begin{aligned} \Delta H_r^\circ &= [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{H}_6)] - [(1 \text{ mol})(\Delta H_f^\circ \text{C}_2\text{H}_2) + (2 \text{ mol})(\Delta H_f^\circ \text{H}_2)] \\ &= [(1 \text{ mol})(-84.68 \text{ kJ mol}^{-1})] - [(1 \text{ mol})(226.73 \text{ kJ mol}^{-1}) + (2 \text{ mol})(0 \text{ kJ mol}^{-1})] \\ &= -84.68 \text{ kJ} - 226.73 \text{ kJ} \\ &= -311.41 \text{ kJ} \end{aligned}$$

(+6 for calculation, -1 math, 1 SF, -1 units)

Exothermic

(+2, okay if consistent with wrong answer above)

(b) (8 points) Calculate  $\Delta S^\circ$  for the reaction. Explain briefly why the sign of your answer makes sense.

Answer:

$$\begin{aligned} \Delta S_r^\circ &= [(1 \text{ mol})(S^\circ \text{C}_2\text{H}_6)] - [(1 \text{ mol})(S^\circ \text{C}_2\text{H}_2) + (2 \text{ mol})(S^\circ \text{H}_2)] \\ &= [(1 \text{ mol})(229.60 \text{ J K}^{-1} \text{mol}^{-1})] - [(1 \text{ mol})(200.94 \text{ J K}^{-1} \text{mol}^{-1}) + (2 \text{ mol})(130.68 \text{ J K}^{-1} \text{mol}^{-1})] \\ &= 229.60 \text{ J K}^{-1} - 462.04 \text{ J K}^{-1} \\ &= -232.70 \text{ J K}^{-1} \end{aligned}$$

(+4 for calculation, -1 MATH, -1 SF, -1 units)

The  $\Delta S^\circ$  for the reaction is positive because there are 3 moles of reactants and 1 mole of product. The system is becoming more ordered. (+4 for answer)

(c) (6 points) Calculate the equilibrium constant K at 298. K to one significant figure. Show all work.

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-311.41 \text{ kJ}) - (298. \text{ K})(-0.23270 \text{ kJ K}^{-1}) \\ &= (-311.41 \text{ kJ}) - (-69.34 \text{ kJ}) \\ &= -242.07 \text{ kJ} \quad +3\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ \ln K &= -\Delta G^\circ / RT \\ \ln K &= -(-242.07 \text{ kJ}) / (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(298. \text{ K}) \\ \ln K &= +97.70\end{aligned}$$

$$\begin{aligned}K &= e^{+97.70} \\ K &= 2.7 \times 10^{42} \\ K &= 3. \times 10^{42} \quad +3\end{aligned}$$

**-1 MATH, -1 SF**

(d) (6 points) Calculate the equilibrium constant K at the higher temperature of 2980 K to one significant figure. Show all work.

$$\begin{aligned}\ln (K_2/K_1) &= -(\Delta H^\circ/R)(1/T_2 - 1/T_1) \\ &= -(-311.41 \text{ kJ}/8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})((1/2980 \text{ K}) - (1/298. \text{ K})) \\ &= (37456 \text{ K mol})((0.0003355 \text{ K}^{-1}) - (0.003355 \text{ K}^{-1})) \\ &= (37456 \text{ K mol})(-0.003020 \text{ K}^{-1}) \\ \ln (K_2/K_1) &= -113.1\end{aligned}$$

$$\begin{aligned}K_2/K_1 &= e^{-113.1} = 7.47 \times 10^{-50} \text{ (no sig figs)} \\ K_2 &= (3. \times 10^{42})(7. \times 10^{-50}) = 2.1 \times 10^{-7} \\ K_2 &= 2. \times 10^{-7} \text{ (accept answer of } 10^{-7} \text{ too, since that is the correct number of sig figs)}\end{aligned}$$

**OR**

$$\begin{aligned}\Delta G^\circ &= \Delta H^\circ - T\Delta S^\circ \\ &= (-311.41 \text{ kJ}) - (2980 \text{ K})(-0.23270 \text{ kJ K}^{-1}) \\ &= (-311.41 \text{ kJ}) - (-690.34 \text{ kJ}) \\ &= +378.9 \text{ kJ}\end{aligned}$$

$$\begin{aligned}\Delta G^\circ &= -RT \ln K \\ \ln K &= -\Delta G^\circ / RT \\ \ln K &= -(+378.9 \text{ kJ}) / (8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1})(2980 \text{ K}) \\ \ln K &= -15.29\end{aligned}$$

$$\begin{aligned}K &= e^{-15.29} \\ K &= 2.3 \times 10^{-7} \\ K &= 2. \times 10^{-7}\end{aligned}$$

**-1 MATH, -1 SF**

(e) (12 points) Calculate the temperature to **two significant figures** at which  $K=1$ , and explain briefly what is true about the spontaneity of this reaction above and below this temperature.

$$\begin{aligned}
 (1/T_2 - 1/T_1) &= \ln (K_2/K_1) / (-)(\Delta H^\circ/R) \\
 &= \ln (1/3. \times 10^{42}) / (-)(-311.41 \text{ kJ}/8.314 \times 10^{-3} \text{ kJ K}^{-1} \text{ mol}^{-1}) \\
 &= \ln (3.33 \times 10^{-43}) / (+37456 \text{ K}) \\
 &= (-97.81) / (+37456 \text{ K}) \\
 ((1/T_2) - (1/298.)) &= - 0.0026113 \text{ K}^{-1} \\
 ((1/T_2) - (0.003355 \text{ K}^{-1})) &= - 0.0026113 \text{ K}^{-1} \\
 1/T_2 &= 0.0007437 \text{ K}^{-1} \\
 T_2 &= 1344.6 \text{ K} \\
 T_2 &= 1300 \text{ K (two sig figs are correct)}
 \end{aligned}$$

OR

When  $K = 1$ ,  $\Delta G^\circ = 0$   
 So  $\Delta H^\circ = T\Delta S^\circ$

$$\begin{aligned}
 T &= \Delta H^\circ / \Delta S^\circ = -311.41 \text{ kJ} / -232.70 \times 10^{-3} \text{ kJ K}^{-1} \\
 T &= 1300 \text{ K (accept five significant figures too if they do problem this way)}
 \end{aligned}$$

+6 for calculations

$T > 1300 \text{ K}$  not spontaneous (+3)

$T < 1300 \text{ K}$  spontaneous (+3)